VOLUME 28 SECOND SERIES NUMBER 3

PERIODICAL ROOM GENERAL LIBRARY U. OF MICH.

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

THE

AMERICAN PHYSICAL SOCIETY

BOARD OF EDITORS

Managing Editor: John T. Tate, University of Minnesota, Minneapolis

R. D. Bardcock, W. G. Cady, E. W. McKeehan, K. K. Darrow, E. C. Kemble, F. L. Mohler, J. A. Eldridge, G. E. M. Jauncey, J. H. Van Vleck

SEPTEMBER, 1926

Luminescence of Pure Barium Bromide under the Action of α, β and γ Rays – Leon E. Smith 431
Energy of X-Rays – – – – – – – – – – – – – – – – – H. M. Terrell 438
Wave-Length Standards in Extreme Ultra-Violet Spectra of C, N, O and Al
– – – – – – – – – – – – – – – – – – – I. S. Bowen and S. B. Ingram 444
Arc Spectrum of Copper – – – – – – – – – – – – – – – – A. G. Shenstone 449
Time Interval between Appearance of Spectrum Lines in Spark and in Condensed Discharges
– J. W. Beams 475
Electronic States and Band-Spectroscopic Structure in Diatomic Molecules. I. Assignment of Postulates, Interpretation of CuH, CuI, and CO Band-Types – Robert S. Mulliken 481
Scattering of Electrons by Ionized Mercury Vapor; Experiments on – – Arthur P. Dittmer 507
Work Function of Oxide-Coated Platinum; Variation with Temperature – Myron S. Glass 521
Secondary Emission from Metals due to Bombardment by High Speed Positive Ions
– W. J. Jackson 539
New Definitions of Electromagnetic Quantities – – – – – – – – – – W. F. G. Swann 531
Theory of Wimshurst's Alternating Current Machine – – – – – – – – A. W. Simon 546
Resistance of the Conducting Layer – – – – – – – – – – – – – G. Breit and M. A. Tuve 554
Magnetic Moments of the Alkali Metal Atoms – – – – – – – – – – John B. Taylor 576
Thermal Conductivity of Li and Na; a Modification of the Forbes Bar Method
– C. C. Bidwell 586
Book Reviews – 598

PUBLISHED BY THE AMERICAN PHYSICAL SOCIETY

MINNEAPOLIS, MINN.

Second Series *September, 1926* *Vol. 28, No. 3*

THE

PHYSICAL REVIEW

THE LUMINESCENCE OF PURE BARIUM BROMIDE UNDER THE ACTION OF ALPHA-, BETA-, AND GAMMA-RAYS

By Leon E. Smith

Abstract

The luminescent material studied (c. p. barium bromide heat-treated) is not luminous by itself, nor is the exciting agent (radium sulphate covered with varnish) self-luminous under the existing conditions. By the use of an especially designed brass capsule the barium bromide was held within the range of action of the α-, β-, and γ-rays from the radium, but the luminescent material and the exciting agent were kept separate. Under these conditions there was for a time, a definite increase in brightness, then from maximum brightness the luminescence decayed with time until a limiting value was reached. Samples of barium bromide from three manufacturers were studied, each under the action of four different amounts of radium. The results were consistent. It was found that the the initial luminosity varies with the temperature at which the barium bromide has been treated previous to the action of the rays. The sample was heated to the desired temperature, then cooled quickly to room temperature, pulverized, placed in the capsule in contact with the radioactive preparation and the brightness measured as soon as possible. The luminosity gradually increased with the temperature of heat-treatment to a maximum value, then the luminescence decreased and rose again to a second maximum, which was followed by a gradual decrease with further increase in the temperature of the heat-treatment through the melting point of the barium bromide.

Introduction

THE decay of luminescence of zinc sulphide due to radium rays has been investigated by several experimenters,[1] and theories have been formulated to explain their results. In the case of barium bromide the initial growth of the luminescence and the variation with the temperature of previous heat-treatment are difficult to explain by these theories.

Przibram[2] and his students while studying photoluminescence in kunzite and other minerals noticed a time variation of the brightness. They found that the luminescence of some minerals increased under the action of β-rays and then gradually decayed after passing through a

[1] E. Rutherford, Proc. Roy. Soc. **83A,** 561 (1909–10); E. Marsden, Proc. Roy. Soc. **83A,** 548 (1909–10); Paterson, Walsh and Higgins, Proc. Phys. Soc. of London **4,** 215 (1917); J. Ewles, Phil. Mag. **45,** 957 (1923).

[2] K. Przibram and E. Kara-Michailova, Akad. Wiss. Wien, Ber. **131,** 2A 285 (1923); **132,** 2A 261 (1924).

maximum. Rodman[3] showed the increase of brightness with the rise in temperature of heat-treatment in the case of pure radium bromide. There appeared one maximum at about 600°C. Karrer and Kabakjian[4] found a variation with temperature as they heated luminescent radium compounds.

Studies in luminescence, up to this time, have been made using mixtures of the luminescent material and the radioactive exciting agent, or the effects have been produced by the use of x-rays, or cathode rays. One of the objects set for this experiment was to keep the source of radiation separate from the luminous material, in order to avoid the formation of any possible complex products. In addition it was thought desirable to use a source of rays that would remain constant through long intervals of time. Under these conditions an attempt was made to investigate the variations with time, and with heat-treatment at different temperatures, of the excited luminescence in pure barium bromide using a deposit of radium salt as the source of the α-, β-, and γ-rays.

Method and Apparatus

An old type Nutting polarization photometer, made by Hilger, was used. The optical system may be represented by the diagram Fig. 1.

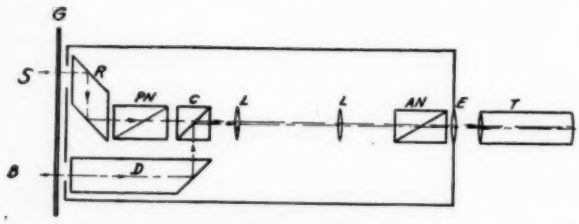


Fig. 1. Diagram of photometer: *S*, standard lamp; *G*, ground glass screen; *R*, reflecting rhomb; *PN* and *AN*, nicol prisms; *C*, photometer cube; *L*, *L*, *E*, lenses; *T*, telescope; *B*, luminescent sample; *D*, reflecting prism.

The standard lamp used was a 110-volt incandescent carbon filament lamp burned at 60 volts. This in turn was compared with two similar lamps calibrated at the Bureau of Standards. Constant lamp voltage was attained by the use of a potentiometer arrangement in a circuit using storage batteries as a source, and a ballast lamp to stabilize the current for small variations in the battery voltage.

The chief difference from other experiments in luminosity lies in the method used to produce the luminescence and at the same time to keep

[3] Miss J. A. Rodman, Phys. Rev. **23**, 478 (1924).
[4] E. Karrer and D. H. Kabakjian, Jour. Frank. Inst. **186**, 317 (1918).

the materials pure and separate. Brass capsules were prepared as shown in Fig. 2, each consisting of four parts. On the face of the thimble (4) was soldered a gold plate upon which was spread a thin layer of radium sulphate. The purpose of the gold plate was to facilitate the recovery of the radium after its use. This layer of radioactive material was covered with a coat of varnish. One coat was usually enough to keep most of the decay products of the radium sulphate underneath and still be thin enough to permit the α-rays as well as the β- and γ-rays to pass through. The radioactivity was tested from time to time and found to reach an equilibrium value which has remained constant for a year. The sleeve (3) served to hold the parts (1) and (4) together. A lead washer (2) provided a means of holding a small amount of barium bromide of a definite thickness in the proper place between the radioactive material and the window in the brass cap (1). A piece of very thin mica covered the luminescent sample and the lead washer. Against this mica disc the

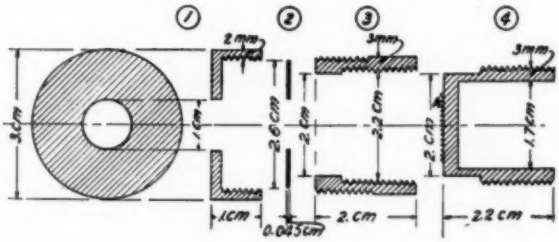


Fig. 2. Brass capsule. 1, a cap; 2, a lead washer; 3, sleeve; 4, thimble; *A*, the radioactive material.

cap (1) was screwed snugly. This arrangement was easy to use, could be kept in a desiccator when not in use, provided a definite thickness of the sample and held it in place. By a series of trials a thickness of sample was found which produced maximum brightness. This thickness, which is about the range of the α-particle in the powdered barium bromide, was then used with exciting sources of 0.3 to 0.9 milligrams of radium in the form of radium sulphate spread over an area of about one square centimeter.

The barium bromide used in these measurements was heated to various temperatures in a hard glass or a quartz tube, allowed to cool quickly to room temperature, then ground in an agate mortar and placed in the capsule in powder form. All measurements were made at room temperature.

The errors involved are those due to personal error in reading very low intensities of light, and those due to the optical system employed.

Results

This study has shown for a pure substance (c.p. barium bromide) what has been observed in mixtures; first, the growth of the brightness to a maximum value as time progresses, followed by the decay of the luminescence with time from this maximum to a constant value; second, the variation of the initial luminosity with the temperature to which the sample has been subjected before exposure to the radium rays.

The luminescence as shown in Fig. 3a gradually grows to a maximum value under the continuous action of the constant source of α-, β- and γ-rays. From this maximum the luminosity gradually decays to a constant value under the action of the same source of rays. The time to reach the maximum brightness varies with the amount of radium present. In Fig. 3a, the barium bromide used was from the same maker, but the

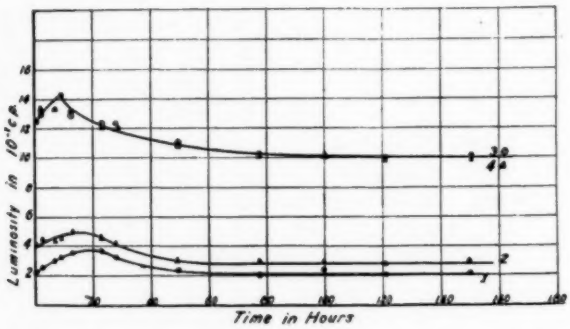


Fig. 3a. Time-luminosity variation. Barium bromide prepared by Mallinckrodt was used for these curves. The number of the curve corresponds to the number of the capsule.

four capsules used carried different amounts of radium in them. Number 1 with the least amount of radium takes the longest time to reach its maximum, and this maximum value is not so great as the maxima in which stronger bombarding sources are used. This shows that the strength of the α-, β- and γ-ray source affects both the brightness of the sample and the time required to reach its maximum luminosity. As the curves are all plotted on the same scale it is seen that the stronger the radioactive source the brighter is the sample throughout the course of the study and the sooner it reaches its maximum value. In curve No. 1 Fig. 3a, the maximum is attained in about twenty hours, with 0.293 milligrams of radium present. In curve No. 2, the time for this maximum is about fourteen hours, with 0.522 milligrams of radium on capsule No. 2. In curves Nos. 3 and 4 in Fig. 3a, where the time required to attain the maximum luminosity is about nine hours, sources of 0.910 and 0.815 milligrams of radium were used on capsules 3 and 4 respectively.

Fig. 3b shows the time-luminosity study using the same capsule (No. 4 in this case) with three different preparations of supposedly pure barium-bromide. Samples from Merck, Mallinckrodt and Kahlbaum show the same general characteristics as to the shape of the curves and the time of reaching the maximum, although the actual values of the brightness at the maximum and the rate of the decay vary somewhat in the different samples. An attempt to purify one of these samples, that from Kahlbaum, by five successive recrystallizations from c.p. hydrobromic acid (Merck) failed to produce any definite change in the luminescence.

A possible explanation of the rise in the luminescence might be assigned to small amounts of the emanation leaking through the varnish and

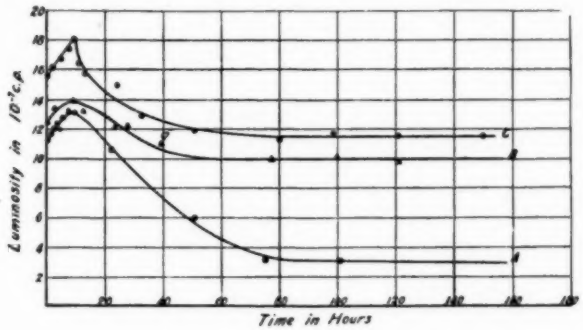


Fig. 3b. Time-luminosity variation. Curve *A*, Kahlbaum barium bromide used in capsule No. 4; *B*, Mallinckrodt barium bromide in No. 4; and curve *C*, barium bromide from Merck in the same capsule, No. 4.

producing luminescence by an active deposit on the salt itself. If this were true, the compound should show considerable luminescence when the source of radiation is removed. This was tested by removing the sample from the capsule and examining it in the dark, but no luminescence comparable to the rise observed in these experiments could be detected. A very feeble luminescence was noticed, which probably was due to a slight degree of thermoluminescence in the material. This effect completely disappeared on heating to about 200°C, showing it could not be due to an active deposit from the radium emanation. As further evidence that escaped emanation cannot be the cause of the effects noticed, the lid of the capsule containing the barium bromide was removed and the compound exposed in a desiccator for a time long enough to allow any emanation that it might contain to diffuse away. On replacing the cap the luminescence had not measurably changed, showing that the growth of the luminescence cannot be explained on this basis.

Long-continued exposure to the radiation causes the barium bromide to acquire a brownish color. This phenomenon has been observed by numerous experimenters before and was noticed in this case also. This brownish-colored barium bromide shows thermoluminescence.

The second result of this study is the change of the luminescence produced by changing the temperature to which the sample is subjected before measurement. The sample was brought to the desired temperature which was measured by a Thwing thermoelectric pyrometer, then removed from the furnace, cooled to room temperature, put into the capsule and the initial luminescence measured. Ordinary unheated pure

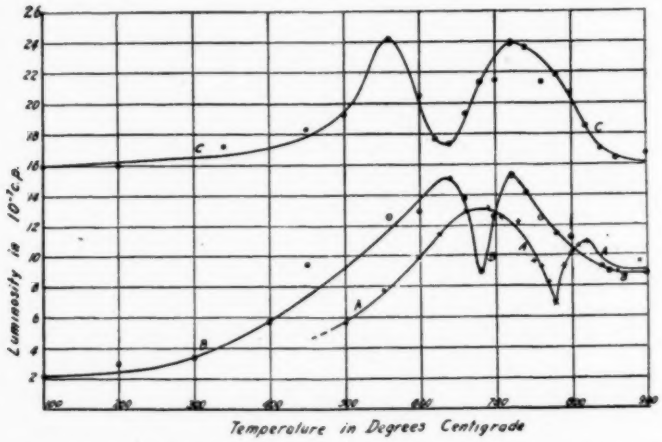


Fig. 4. Initial luminosity plotted against the temperature of the heat-treatment previous to exposure to the radium rays. Capsule No. 4 used in every case. Curve *A*, a sample of Kahlbaum; *B*, Mallinckrodt; *C*, Merck was used.

barium bromide does not show appreciable luminescence under the action of the α-, β- and γ-rays. After heating at 100°C the luminescence which is excited by the sources used is barely measurable. With slightly higher temperature the barium bromide gives up its water of crystallization, with no sudden change in the luminosity. No progressive change in the initial luminosity could be detected by continuous heating at a constant temperature of 290°C for a week. With higher temperatures the luminescence rises gradually until it reaches a maximum, for Mallinckrodt material at about 650°C. More intense heating results in a sudden drop in the brightness. This decrease is followed by a sharp rise in the luminescence until a second maximum is reached, at about 750°C for Mallinckrodt material. From this point the initial luminescence falls off at least until the melting point is passed. There seems to be no sudden change in the luminescence due to fusion during the heat-treatment. Fig. 4 shows the results of such a temperature study of luminescence

using the same source of radiation, capsule No. 4, and the three samples of barium bromide, Merck, Mallinckrodt and Kahlbaum. The number of inflection points and the general shape of the curves are the same in all cases, although the maxima and the minima are reached at different temperatures, and the brightness varies somewhat from sample to sample. It is proposed to continue the study of these variations in the luminescence with previous heat-treatment.

There is no point of inflection nor discontinuity in the curves near the temperature at which the water of crystallization disappears, nor does there seem to be such point at the fusion temperature, 880°C. The duration of the heat-treatment seems to have no effect. After a few minutes exposure at a given temperature, no difference can be found between the resultant initial brightness and that after the sample has been heated at this same temperature for days.

The barium bromide which has been exposed to the radiations appears to recover its initial properties on heating to 700°C or more. There is no observable difference in the variations of luminosity with temperature between samples which have been exposed to α-, β- and γ-rays for weeks and samples which have not been so exposed, provided they have been adequately heated.

If luminescence is explained by the destruction and the recovery of the active centers, this experiment shows that the α-, β- and γ-rays must have something to do with the production of these active centers as is indicated by the initial rise of luminescence as well as the destruction of the centers resulting in the decay which is always observed. These studies seem to add weight to Perrin's[5] assumption, that the luminescence must be affected by the bath of radiation in which the luminescing material is placed. He assumed that the radiation must also affect the recovery process. Witmer[6] using Perrin's hypothesis derived an equation to explain the facts found in Rodman's paper on the luminescence of pure radium bromide. Witmer's equation in its present form does not seem to fit the results of this study on pure barium bromide. To make this theory satisfy luminescence in general some revision must be made in it.

The writer wishes to acknowledge his indebtedness to Professor D. H. Kabakjian for his suggestions and his help in this studv.

RANDAL MORGAN LABORATORY OF PHYSICS,
UNIVERSITY OF PENNSYLVANIA,
June 10, 1926.

[5] J. Perrin, Ann. de Physique **11**, 5 (1919).
[6] E. E. Witmer, Phys. Rev. **24**, 639 (1924).

THE ENERGY OF X-RAYS

By H. M. Terrill

Abstract

An apparatus is described to determine the total energy of x-rays from a tube by the conversion of this energy into heat. The x-rays are absorbed in a lead coil connected with a resistance thermometer bridge, and the amount of heat developed is determined from the current that must be passed through the coil to give the same temperature rise. The energy thus found is compared with the power input to determine the efficiency of the production of x-rays.

A tungsten target tube is excited by constant potential direct current at from 30 to 100 KV and the energy per unit solid angle is found to be 39 to 305×10^{-6} times the power supplied. This corresponds to an approximate total output of the tube of .00025 to .00192 times the input for the same range of voltages. Plotted against the square of the voltage these values give a straight line to 69.3 KV where a change of slope occurs, probably due to the selective absorption of the target itself.

Purpose of the Investigation

THE purpose of the present investigation is to measure the total x-ray energy output of an x-ray tube by the conversion of this energy into heat. The energy thus found is compared with the power input to determine the efficiency. This problem is comparatively old, and a valuable summary of the early results is given by Weeks.[1]

In view of the importance of the problem, it is desirable to repeat and extend the measurements, using a tube excited with constant potential direct current. The voltage may be then measured directly by means of a high resistance multiplier. The power supplied the tube is subject to precise control and measurement, and furthermore the quality of the x-rays obtained is independent of any wave form.

Water-cooled Coolidge tubes are used, not only minimizing the possibility of heat leakages into the measuring apparatus, but also permitting higher current to be used with consequent increase in sensitivity.

Method

A bolometer, or resistance thermometer method is employed, the x-rays being converted into heat by absorption in lead. One of a pair of lead wire coils is exposed to x-rays, and the temperature rise determined by its change in resistance, the other coil occupying the opposite arm of the thermometer bridge for compensation. The amount of heat received from the x-rays is then determined by measuring the current that must be passed through the coil to give the same temperature rise.

[1] Weeks, Phys. Rev. **10**, 564 (1917).

The coils must be constructed so as to have as high a resistance as possible to insure sensitivity, and yet contain just sufficient lead to absorb all the x-rays that fall on them. This condition is secured by using a rather fine wire, No. 26 single silk-covered being about as fine as is convenient to wind.

The general shape and arrangement is shown in Fig. 1. The coils are of the pancake type, about 5 cm in diameter, and .28 cm thick and have a 1 cm hole in the center. They are wound to a resistance of 36 ohms per coil. The weight of one of the coils is 32 gm or 1.6 gm per cm^2 of area. That this is sufficient to absorb all radiation up to 100 KV is shown by the fact that no further increase is obtained by the use of a coil 30 percent thicker.

To shield the coils from outside radiation and to insure that temperature changes in the surroundings will affect them both equally, they are enclosed in a lead lined housing of heavy sheet brass with aluminum

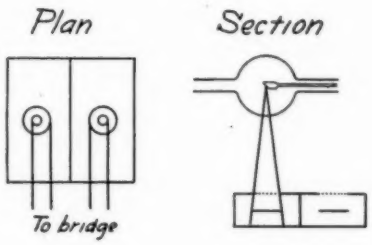


Fig. 1. Apparatus in position beneath x-ray tube.

windows. Save for the actual path of the beam of x-rays, the space within the housing is filled with wool batting, upon which the coils rest, separated by a lead partition. The windows are made of two sheets of .002 cm aluminum foil separated by a .5 cm air space, and there is also in the path of the rays another sheet of the same foil close to the tube, as well as a sheet of lens paper, both of which serve to cut down air currents. Thus, the total amount of material between the coil and the tube probably does not amount to more than 10 percent of the wall of the tube itself. The tube is contained in a lead covered box through which air is continuously circulated by a powerful blower. The efficiency of the shielding is high, blank runs being made to show that the bridge balance is not affected by temperature changes in the outside room, heat from the filament of the x-ray tube, nor from the body of the observer.

Extra precautions are taken to secure accuracy in measuring the distances of the coils and ionization chamber from the target of the tube. Pinhole photographs of the target are first made to locate the position of

the focal spot, and the distance from the center of the focal spot to the measuring device is then determined with the aid of a cathetometer. A fluoroscope is used to center the measuring coil under the x-ray tube and to adjust diaphragms to limit the beam, so that, while the coil is completely radiated, very little radiation gets past its edges to cause error by scattering back upon it.

Some time before readings are made, the windows before the coils are closed by lead shutters, the x-ray tube switched on, and temperature conditions allowed to come to equilibrium. The bridge being balanced, if x-rays are allowed to fall upon one of the lead coils by opening the shutter, the galvanometer starts to move and, with an intense beam of x-rays, would in a minute or so be entirely off the scale unless resistance is continually cut in by means of the slide wire.

To determine the heat collected, the coil is radiated for a period of five minutes, readings being taken on the galvanometer or slide wire at half-minute intervals, after which the x-rays are shut off and the coil allowed to cool. It is then disconnected from the bridge by a mercury switch and current passed through it of such value, found by trial, as to give the same galvanometer deflections or slide wire readings within the same time intervals. The energy, computed by the I^2R relation, is assumed to be equal to the energy of the x-rays.

The total measuring current used is .012 amperes and is switched on for each reading only long enough to permit the galvanometer to come to rest, thus avoiding unnecessary heating of the coils.

Total Energy as a Fraction of the Input

A measurement of the energy of a definite quantity of x-rays implies that this definite quantity of x-rays is determined by some other method. There are two methods commonly used.

The heat energy may be determined as a fraction of the power supplied to the tube, thus leading to an idea of efficiency. This fraction is a function of the voltage and the measurements should be extended over a range of voltages. On the other hand, the heat energy may be measured of a beam of x-rays whose intensity has been determined by an ionization method. This leads to a determination of the ratio of ionizing effect to energy and the ratio being a function of the wave-length, the measurements should be made with monochromatic rays, and over a range of wave-lengths. Both methods are employed in the work with this apparatus and will be treated in separate articles.

For measurements of the total energy as a fraction of the input, which is the subject of the present investigation, a tungsten target tube is used.

The radiated coil is held at 27.3 cm from the target and subtends .027 units of solid angle, or 1/466 of the whole sphere.

The voltage is varied upward from 30 KV in steps of 10 KV. The current is adjusted so as to keep the output approximately constant. While preliminary runs show that the energy collected is proportional to the current through the tube, it is advisable to make all readings at approximately constant output. The lead coil then receives the same amount of heat each time, and errors due to heat losses, etc., affect only the absolute value of the results. In these measurements, this amount of heat is 39×10^5 ergs in a five minute period.

In Table I is listed for each voltage the fraction of the input radiated in unit solid angle. The third column gives the product of these values and 2π, being the energy that would be radiated were the intensity uniform over the lighted hemisphere. This is an approximation to the total amount of x-ray energy actually radiated from the tube. The next column gives the preceding multiplied by 2, giving approximately the total amount of x-rays produced at the target, including the energy in the dark hemisphere that is absorbed by the metal of the target.

TABLE I

Data on efficiency of x-ray tube

Voltage *KV*	Fraction of input in unit solid angle	Col 2 $\times2\pi$	Col 2 $\times4\pi$
30	39×10^{-6}	.00025	.00050
40	68 "	.00043	.00086
50	96 "	.00061	.00122
60	137 "	.00086	.00172
70	179 "	.00112	.00224
80	215 "	.00135	.00271
90	260 "	.00163	.00326
100	305 "	.00192	.00384

To investigate the general law followed by the values in column 2, they are plotted against the square of the voltage at *A* in Fig. 2. Up to 69 KV they lie quite closely on a straight line, there being but a slight deviation from this at the extreme low voltage end.

No corrections are made for the absorption in the walls of the tube. To throw further light on this point, the readings are repeated with interposed filters of one to three sheets of half millimeter aluminum, one of these sheets being roughly equivalent to the wall of the tube. The curves *B*, *C*, and *D* of Fig. 2 show the effect of these filters. It is seen that the filters have little effect on the general shape of the curve, all the points being lowered proportionately. Hence, by assuming that the wall of the tube has approximately the same effect as one of these

filters, a visual estimate may be made as to what the curve would be, corrected for the absorption of the wall.

A downward change of slope occurs between 60 and 70 KV similar to an effect observed in the case of silver by Brainin.[2] A possible explanation for this may be found in the filtering action of the target itself. The face of the target stands at an angle of 70° to the direction of the cathode and 20° to that of the measuring apparatus. Hence, in all cases, the x-rays pass through more than twice as much tungsten as the cathode rays that produced them and this distance may be enormously increased by the presence of small pits and scratches in the face of the target. The sudden increase of the absorption above the K limit would thus affect the radiation produced at voltages over 69.3 KV, and so account for the change of slope at this point.

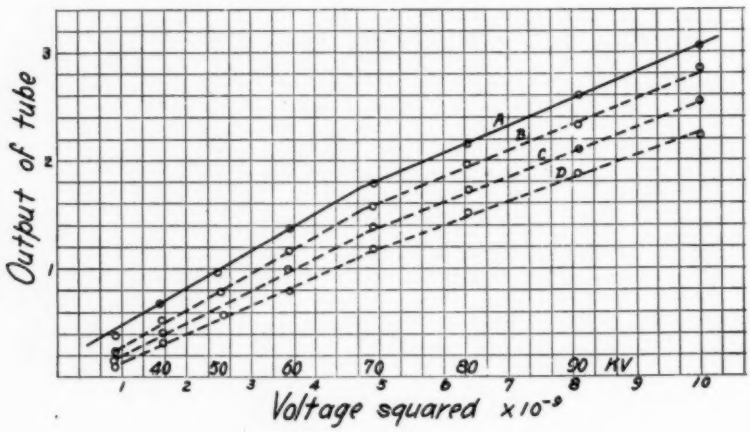


Fig. 2. Output as a function of the square of the voltage. The dotted lines represent effect of aluminum filters.

If this explanation be correct, the effect should decrease if the target stand at a sharper angle to the beam of cathode rays or the radiation be measured in a direction nearer the normal to the surface of the target. It is hoped to investigate this point in further experiments.

The present results are in agreement with the work of Ulrey[3] who found, by integrating curves obtained with a spectrometer, that the total emission of tungsten was proportional to the voltage squared, between the limits 20 and 50 KV.

[2] Brainin, Phys. Rev. **10**, 461 (1917).
[3] Ulrey, Phys. Rev. **11**, 401 (1918).

There is also very good agreement in absolute value with the results of Weeks,[4] who worked from 28 to 54 KV. It should be pointed out that x-ray tubes differ in output and too much importance should not be attached to exact agreement of the absolute value.

As shown by Coolidge,[5] a certain proportion of the radiation comes from the back and stem of the target, due presumably to electrons reflected or splashed out of the face, and this proportion may vary with the size and shape of the target, the cathode distance, the size of the focal spot, and the size and shape of the glass bulb, and even with the location of surrounding external objects such as shields and supports in so far as they affect the field within the tube.

The condition of the surface of the target as well as the angle at which it is inclined to the beam of cathode rays are also factors of the efficiency, a pitted or cracked surface increasing the filtering effect due to the target itself, and so decreasing the amount of energy radiated.

The absolute value of the efficiency is thus seen to be dependent to a certain extent upon the design and condition of the tube. To estimate how closely the present values approximate the ideal efficiency requires a rather elaborate discussion which will be made the subject of a future article in which it is hoped also to extend these results to higher voltages.

Besides comparing the total energy with the power input, it may be compared with the ionization in air. This work is at present partially completed and the results will be published shortly.

This series of investigations of the energy of x-rays were undertaken at the suggestion of Dr. Francis Carter Wood, and have been made possible by his development of a high voltage x-ray laboratory.

INSTITUTE OF CANCER RESEARCH,
COLUMBIA UNIVERSITY,
June 15, 1926.

[4] Weeks, *loc. cit.*, p. 570.
[5] Coolidge, Am. Jour. Roent. **2,** 882 (1915).

WAVE-LENGTH STANDARDS IN THE EXTREME ULTRA-VIOLET SPECTRA OF CARBON, NITROGEN, OXYGEN AND ALUMINUM

By I. S. Bowen and S. B. Ingram

Abstract

Wave-length determinations.—The wave-lengths of lines in the extreme ultra-violet spectra of carbon, nitrogen, oxygen and aluminum have been determined with an accuracy of .01 to .04A by direct comparison with iron standards.

pp′ groups in carbon C_{III} and nitrogen N_{IV}—pp′ Groups of carbon C_{III} and nitrogen N_{IV} have been completely resolved into six components and the ratio p_1p_2/p_2p_3 found to be 2.47 and 2.33 respectively.

1. Determination of Wave-Lengths

IN a preceding article[1] by Dr. Millikan and one of the authors wave-length standards in oxygen and nitrogen were published. For these earlier determinations the strong aluminum lines between 1850A and 2000A served as primary standards. In the course of subsequent studies it has become increasingly evident that the wave-lengths of these aluminum lines were inconsistent with themselves, one of the doublet separations being in error by as much as .17A. The present paper presents an attempt to eliminate this source of error by bringing high orders of strong lines in the extreme ultra-violet into direct comparison with first order iron lines. This standardization has also been carried to carbon and aluminum as well as to the nitrogen and oxygen reported in the earlier article, thus providing a set of standards completely covering the range from 600A to 2000A.

For this purpose the spectrum of a vacuum spark between one aluminum and one iron electrode was photographed in various regions between 3000A and 6000A. As has been noted previously such a spark brings out the carbon and oxygen lines strongly in addition to those of aluminum and iron.

In the determination of wave-lengths the first step was the calculation of approximate values on the assumption of a linear relationship between the position on the plate and the wave-length. Using these approximate values all iron lines appearing on the plate were identified and the difference between their true and approximate wave-lengths determined. Plotting these deviations against the wave-length gave a curve which

[1] Bowen and Millikan, Phil. Mag. **48**, 259 (1924).

could be used in correcting the approximate wave-lengths of all other lines on the plate. In general this correction did not exceed one angstrom.

The various values of the wave-lengths of the oxygen, carbon, and aluminum lines were weighted as to order, sharpness of the line, and nearness to iron standards, and then averaged. As a further check on their mutual consistency and on the doublet separations the values thus determined were compared with the data obtained from a number of high order plates that had been taken for other purposes. Some slight adjustments were made to correct a few discrepancies brought to light by this comparison, but in no case was this adjustment greater than the indicated possible error in the wave-length (see below).

The best of the plates compared was that of a spectrum of a vacuum spark between aluminum electrodes containing sodium nitrate. The wave-lengths of the lines on this plate had previously been determined by means of a large number of first order oxygen lines occurring on it. The comparison with our carbon, oxygen, and aluminum standards indicated a systematic error of about .04A in this previous determination. After correcting for this small error the data from this plate were used for the determination of the nitrogen standards.

A test of the accuracy of the fine structure separations can be obtained by comparison of related series lines and pp' groups. Thus, an error of about .01A in any one of the four lines involved would account for the difference between the doublet separations of 1854A and 1379A, and errors of from .006A to .009A would account for all discrepancies in the pp' groups at 685A, 922A and 1175A. It is also possible to check the absolute values of certain lines. Thus, the frequency of the 1935A line

TABLE I

Int.	λ I. A. Vac.	ν	Accuracy	Int.	λ I. A. Vac.	ν	Accuracy
			Carbon				
5	977.031	102350.9	B	2	1247.391	80167.3	C
1	1009.863	99023.3	B	5	1334.541	74932.1	B
1	1010.095	99000.6	B	5	1335.703	74866.9	B
1	1010.383	98972.4	B				
				5	1548.189	64591.6	A
2	1036.339	96493.5	A	4	1550.774	64483.9	A
2	1037.018	96430.3	A				
				2	1560.257	64092.0	B
3	1174.922	85112.0	A	3	1560.660	64075.5	B
3	1175.261	85087.5	A	3	1561.378	64046.0	B
2	1175.577	85064.6	A				
4	1175.711	85054.9	A	4	1931.027	51785.9	B
3	1175.988	85034.9	B				
3	1176.359	85008.1	A				

TABLE I (Continued)

Int.	λ I. A. Vac.	ν	Accuracy	Int.	λ I. A. Vac.	ν	Accuracy.
			Nitrogen				
3	685.000	145985.4	A	4	989.802	101030.3	B
3	685.517	145875.3	A	4	991.570	100850.2	B
4	685.822	145810.4	A				
3	686.346	145699.1	A	5	1083.956	92254.7	B
				5	1084.529	92205.9	B
3	763.348	131001.8	C	3	1085.497	92123.7	C
3	764.358	130828.7	C	6	1085.688	92107.5	C
3	765.158	130692.0	C				
				2	1134.180	88169.4	B
1	771.542	129610.6	B	3	1134.420	88150.8	B
2	771.914	129548.1	B	3	1134.987	88106.7	B
2	772.398	129466.9	C				
1	772.938	129376.5	C	3	1199.533	83365.8	B
				2	1200.200	83319.4	B
3	915.595	109218.6	B	1	1200.681	83286.1	C
4	915.986	109172.0	B				
4	916.690	109088.1	B	0	1740.315	57460.9	C
				3	1742.740	57380.9	B
2	921.978	108462.5	B	3	1745.260	57298.1	B
2	922.512	108399.7	B	2	1747.855	57213.0	B
1	923.037	108338.0	B				
3	923.211	108317.6	B				
2	923.658	108265.2	B				
2	924.264	108194.2	B				
			Oxygen				
2	599.600	166777.9	B	2	796.665	125523.3	B
2	702.329	142383.4	A	4	832.754	120083.5	A
2	702.813	142285.4	A	3	832.924	120059.0	A
2	702.905	142266.7	A	4	833.327	120000.9	A
3	703.850	142075.7	A	4	833.739	119941.6	A
				5	834.459	119838.1	A
3	718.522	139174.6	B	3	835.099	119746.3	A
				5	835.288	119719.2	A
1	779.824	128234.1	B				
2	787.716	126949.3	B				
2	790.205	126549.4	B				
			Aluminum				
2	1352.857	73917.6	A	4	1760.101	56814.9	A
				4	1761.973	56754.6	A
4	1379.675	72480.8	B	5	1763.939	56691.3	A
4	1384.140	72247.0	B	4	1765.814	56631.1	A
				4	1767.730	56569.7	A
7	1605.764	62275.7	B				
7	1611.858	62040.2	B	10	1854.715	53916.6	B
				10	1862.775	53683.4	B
6	1670.802	59851.5	C				
				6	1935.881	51656.1	B
4	1719.455	58158.0	A				
5	1721.273	58096.5	A	4	1990.534	50237.8	B
5	1724.982	57971.6	A				

and the difference in the frequencies of the lines at 1605A and 1379A can be calculated from series relationships. In both of these cases the error does not exceed .003A.

The intensities and final wave-lengths are given in the first two columns of Table I. A letter *A* in the fourth column indicates that the line can probably be depended upon to .01A, *B* indicates .02A, and *C* .03A or .04A.

2. The pp' Groups in Carbon C_{III} and Nitrogen N_{IV}

Among the lines studied in the above work were the pp' groups of carbon C_{III} and nitrogen N_{IV} which were here for the first time completely resolved into their six components as shown in Table II. This enables us to determine the ratios of the separations of p_1p_2 and p_2p_3 which are given in Table III together with all previous determinations in related

Table II

pp' Groups in two-valence-electron atoms

Carbon C_{III}

		p_1		p_2		p_3	
Int.	:			(3)			
λ	:			1175.988			
ν	:			85034.9			p_3'
$\Delta\nu$	:			29.7			
Int.	:	(3)		(2)		(3)	
λ	:	1176.359		1175.577		1175.261	
ν	:	85008.1	56.5	85064.6	22.9	85087.5	p_2'
$\Delta\nu$	:	46.8		47.4			
Int.	:	(4)		(3)			
λ	:	1175.711		1174.922			
ν	:	85054.9	57.1	85112.0			p_1'

Nitrogen N_{IV}

		p_1		p_2		p_3	
Int.	:			(2)			
λ	:			923.658			
ν	:			108265.2			p_3'
$\Delta\nu$	:			72.8			
Int.	:	(2)		(1)		(2)	
λ	:	924.264		923.037		922.512	
ν	:	108194.2	143.8	108338.0	61.7	108399.7	p_2'
$\Delta\nu$	:	123.4		124.5			
Int.	:	(3)		(2)			
λ	:	923.211		921.978			
ν	:	108317.6	144.9	108462.5			p_1'

TABLE III

Ratio of the triplet separations p_1p_2/p_2p_3

	2*p*	3*p*
Be_I	3.57	
B_{II}		
C_{III}	2.47	2.33
N_{IV}	2.33	
O_V	2.27	

elements. It is at once seen that in going to elements of higher atomic number this ratio approaches the value 2 called for by Landé's interval rule.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA.
June 8, 1926.

THE ARC SPECTRUM OF COPPER*

By A. G. Shenstone

Abstract

The arc spectrum of coppper is partly an ordinary doublet spectrum with lowest term $^2S=62308.0$; and partly a complicated spectrum with lowest term $m^2D_3=51105.5$ and $m^2D_3=49062.6$. The next lowest terms of the complicated spectrum are ^4P, ^4F, ^4D,' ^2F, ^2P, $^2D'$ in the order given extending from $^4P_3=23289.4$ to $^2D'_3=15709.7$. They combine with ^2S and m^2D. The quartets are all inverted, while the doublets are not. There are eleven higher terms which include amongst others a second set ^2F, ^2P, $^2D'$. This is all as predicted by the Heisenburg-Hund theory. Most of the lines of the arc spectrum are due to the combinations of the above quartets and doublets with a set of terms having negative wave-numbers extending from -95.2 to -14772.4. In particular, the lowest four negative terms are a complete ^4D and form by combination with ^4P, ^4F, $^4D'$ multiplets of great intensity in the visible. The other negative terms include a set ^4S, $^4P'$, ^4D, $^4F'$, ^4G, which also combine with considerable intensity with the first mentioned quartets. The limit of the negative quartet terms can be calculated to be at roughly $-22{,}000$. This should be the lowest spark ^3D term.

The nature of the quartet spectrum was partly determined from Zeeman effects in the ultra-violet below 2500. The g-values of many of the terms are irregular but the g-sums are correct. Line intensities were used mainly as criteria for the designation of terms. Unresolved Zeeman effects give confirmation in many cases.

The two types of spectra are connected by combinations of the lowest terms of each with higher terms of the other. Other theoretically possible combinations do not occur.

THE spectrum of copper has long been known to contain term sequences of ordinary doublet type.[1] The lowest term is a ^2S term 62308.0, and there are known, in addition, a number of P, D, and F terms. This spectrum is discussed below.

There exist also two ^2D terms whose abnormally low values prevent their inclusion in the ordinary D-sequence. They have wave numbers $m^2D_2=49062.6$ and $m^2D_3=51105.5$ and are thus inverted. The combinations of all of the above terms account for only about 45 lines of the 500 or more known to be due to the copper atom. In a recent paper[2] the

* After this paper had been written, there was received a paper by C. S. Beals "Quartet terms in the arc spectrum of copper" (Proc. Roy. Soc. A **111**, 1926). By the aid of Zeeman effects Beals has discovered the main set of quartet terms comprising the low ^4P,$^4D'$,^4F and the higher ^4D with which they combine. The two papers are in complete agreement on this most important point, except that Beals has observed the one line λ 4069 which is missing in the tables. Beals' evidence for the classification of the quartet terms is probably more conclusive than the author's.

[1] A. Fowler, "Report on Series in Line Spectra."

[2] A. G. Shenstone, Phil. Mag. **49**, 952 (1925).

author has shown that this complex part of the spectrum is intimately connected with the terms m^2D.

A large part of the spectrum has now been analysed, and a comparison is made below between that analysis and the results predicted by the very successful theory developed by Pauli,[3] Heisenberg,[4] and Hund,[5] on the basis of the conclusions of Russell and Saunders[6] from the calcium spectrum.

The copper ion in its lowest state should consist of an electron configuration which can be represented as d^{10}, where the index indicates the number of electrons in orbits whose k-values are given by the letters s, p, d, etc. The inner closed shells of electrons are omitted for convenience. This state is a ^1S term, on which would be built by the addition of one electron the ordinary doublet spectrum of the atom. Another possible condition of the ion is d^9s. The composition of the quantum vectors of the separate electrons in such a configuration can be shown to result in any one of the four terms included under the notation ^3D and ^1D. The addition of a further s-electron yields terms of the atom ^4D, ^2D, ^2D, which, due to Pauli's equivalent electron principle, merge, in the lowest state (d^9s^2) into a ^2D alone. This term should be inverted and very low and is, undoubtedly, m^2D referred to above. It should be the leading member of two series of ^2D terms, one of which should converge to the spark ^1D and the other to two components of the spark ^3D term. The ^4D terms should have as limit the ^3D spark term.

The next lowest terms of the atom should be given by the addition of a p-electron to d^9s, namely d^9sp. This configuration can be shown to give terms ^4P, $^4D'$, ^4F, ^2P, $^2D'$, ^2F, based on the spark ^3D, and ^2P, $^2D'$, ^2F, based on the spark ^1D. From empirical rules deduced from other spectra, the quartets should be the lowest terms. All the above terms should combine with m^2D and ^2S where the j-selection principle permits. Some of these terms have already been found from the absorption experiments of Zumstein,[7] the author (loc. cit.), and McLennan and McLay.[8] The remainder of the quartets and lower doublets have now been identified from their combinations, as well as a further eleven terms which probably include the second set of doublets originating from the spark ^1D, as well as terms which belong to the electron configuration d^8s^2p.

[3] W. Pauli, Jr. Zeits. f. Physik **31,** 765 (1925).
[4] W. Heisenberg, Zeits. f. Physik **32,** 841 (1925).
[5] F. Hund, Zeits. f. Physik **33,** 345 (1925).
[6] H. N. Russell and F.A. Saunders, Astrophys. J. **61,** 38 (1925).
[7] R. V. Zumstein, Phys. Rev. **25,** 523 (1925).
[8] J. C. McLennan and A. B. McLay, Trans. R. S. Can. **19,** 89 (1925).

TABLE I

Term	Type	Intervals.	$^2S_1$ 62308.0	m^2D_1 49062.6	m^2D_2 51105.5	No. of Comb.
23289.4	a^4P_3			———	27816.1 (2)	15
		1095.4				
22194.0	a^4P_2		40114.0 (8)	26868.5 (2)	28911.4 (3)	16
		829.7				
21364.3	a^4P_1		40943.9 (6)	27698.3 (2)		7
21398.9	a^4F_5					5
		244.3				
21154.6	a^4F_4				29950.8 (6)	17
		409.4				
20745.2	a^4F_3			28317.4 (6)	30360.5 (2)*	18
		739.7				
20005.6	a^4F_2		42302.6 (1u)	29057.1 (3)	———	13
18794.1	a^4D_4'				32311.3 (6)	19
		892.3				
17901.8	a^4D_3'			31160.8 (4)	33203.7 (5)	19
		137.9				
17763.9	a^4D_2'		44544.3 (2)	31298.7 (6)	33341.6 (2)	18
		371.6				
17392.3	a^4D_1'		44915.9 (2R)	31670.3 (3)		9
18581.9	a^2F_3			30480.7 (3)?	32523.6 (4)	18
		1237.1				
17344.8	a^2F_4				33760.5 (6)	13
16487.2	a^2P_1		45821.2 (1u)	32575.4 (4u)		8
		58.4				
16428.8	a^2P_2		45879.3 (1u)	32633.8 (6)	34676.7 (4)	15
16135.2	a^2D_2'		46172.7 (1u)	32927.4 (6)	34970.2 (2)	14
		425.5				
15709.7	a^2D_3'			33353.0 (4)	35395.7 (8)	15
12925.0	3^2P_2		49383.0 (Calc) 2^2S_1 (combs.)	36137.6 (8)	38180.2 (10r)	3
7523.9	e_3'			41538.7 (6)	43581.4 (8R)	2
7280.3	d_2'			41782.3 (8r)	43825.1 (2)†	4
6278.3	b^2F_4				44827.1 (6R)	9
5964.7	c_2'	621.6	13206.3 (5)	43098.1 (4)	45141.0 (6R)	8
5656.7	b^2F_3			43405.7 (6)	45448.6 (2)‡	10
5027.3	b_4'				46078.4 (2u)	3
4889.4	a_1'		14281.7 (1u)	44173.3 (6R)		3
4358.8	b^2P_2	414.5	14812.3 (2u)	44704.0 (1u)	46747.0 (1u)	4
4188.7	b^2D_2'	571.5		44874.0 (6R)	46916.7 (1)	6
3944.3	b^2P_1		15226.8 (3u)	45118.8 (4R)	47157.7 (0)†	4
3617.2	b^2D_2'		15553.7 (1)	45445.3 (2)‡	47488.1 (0)‡	10

* Kayser † Pina ‡ Author

All of these terms are given in Table I together with their combinations with ^2S and m^2D. Small letters have been prefixed to the term designations in order to distinguish between terms of the same type. The wave lengths are mainly Hasbach's, but in the region below λ2300 they

have been corrected by the use of Mitra's[9] standards, omitting his determination of λ2148 which is almost certainly incorrect.

The nature of several of the terms of Table I was determined by observations of Zeeman effects in the ultra-violet, using for the purpose a Hilger E1 quartz spectrograph. With this instrument simple patterns such as are given by terms of $j=1$ or 2 combining with ^2S are resolvable if the source produces sufficiently fine lines. Most of the copper arc lines are known to be diffuse; and, in the ultra-violet, most of them, being ^2S and m^2D combinations, are wide reversed lines. This difficulty was surmounted without the trouble of a vacuum source by using an iron or zinc anode and copper cathode. Zinc was found to be particularly efficient in reducing the width of the copper lines, even the resonance lines λ3247 and λ3274 appearing in fine emission. In the early work the iron lines served as standards of Zeeman separations. Hilger Schumann plates were used, and with them, exposures rarely exceeded five minutes. A quartz double image prism was made use of to obtain both polarisations on the plate simultaneously. The magnetic field obtained was about 25,000 gauss.

The results obtained for the 1^2S_1 combinations are given in Table II.

TABLE II

λ	Designation	Zeeman Pattern	g (calc)	g (Landé)
2492.142	$1^2S_1 - a^4P_2$	±(0) 1.69a	1.7?	$\frac{26}{15}$
2441.625	$1^2S_1 - a^4P_1$	(0) 2.34a	2.68	$\frac{8}{3}$
2244.24	$1^2S_1 - a^4D_2'$	(.45) .$\overline{66}$ − a	1.10	$\frac{6}{5}$
2225.665	$1^2S_1 - a^4D_1'$	(.91) 1.11a	.20	0
2181.71	$1^2S_1 - a^2P_1$	(.77) 1.21a	.44	$\frac{2}{3}$
2178.95	$1^2S_1 - a^2P_2$	(.43) .$\overline{70}$ 1.5a	1.14	$\frac{4}{3}$
2165.10	$1^2S_1 - a^2D_2'$	(.45) .$\overline{66}$ − a	1.10	$\frac{4}{5}$

The Zeeman patterns obtained for the two lines λ2492 and λ2442 leave little doubt that they are $^2S - ^4P_2$ and $^2S - ^4P_1$. The terms $\nu = 22194.0$ and 21364.3 have, therefore, been designated a^4P_2 and a^4P_1. The designation of the term $\nu = 23289.4$ as a^4P_3 is based on the evidence of other combinations which are given below. The failure to observe the line $m^2D_2 - a^4P_3$ is due to two facts. It is theoretically a very faint line; and its position at λ3878.9 is in the midst of very strong nitrogen bands which it has been found impossible to eliminate. An arc in 99% argon gave these bands in great strength as did also an arc in carbon dioxide. A very small amount of nitrogen is evidently sufficient for the appearance of these bands.

[9] Mitra, Ann. d. Physique **19**, 315 (1923).

There is evidence for the identification of the four terms given as ^4F from three sources; unresolved Zeeman effects, some complete patterns communicated to me by Mr. Loring of Harvard University, and intensities of combinations. The line λ2363.20, $^2S-a^4F_2$, is extremely faint and has never appeared on plates of the Zeeman effect. The combination line $mD^2_3-a^4F_2$, theoretically a very faint line, is missing from the tables. A line in the correct position has been measured by the author, but there is a possibility that this is a band line. There is a difficulty in the line $m^2D_3-a^4F_3$. Hasbach's wavelength 3292.903* gives a wavenumber in error by +.7 and Kaiser's value gives an error of −.2. There is good evidence, however, that this is really a double line with a wave number difference of about 1.2, the other member of the pair being a a^4F_5 combination.

The remainder of the resolved patterns yield g-values for the terms involved which are in disagreement with Landé's values. This is, undoubtedly, due to the fact that the spectrum is of the "second rank," i.e. it is produced by atoms in which two electrons are neither in s-orbits nor in closed groups, the lack of one electron from the M-shell in this case being equivalent spectroscopically to the presence of one d-electron.

The magnetic splitting of the line λ2225 allows the calculation of g=.20 for the term $\nu=17392.3$. This is closer to the theoretical value zero for $^4D'_1$ than to the g of any other term with $j=1$. There is little doubt of the designation $^4D'_2$ for $\nu=17763.9$ but there is a real difficulty involved in the choice between 17901.8 or 18581.9 for $^4D'_3$. The unresolved patterns of the lines λ3010 and λ3073 are practically identical; as are also those of the lines λ3208 and λ3279. An examination of the m^2D combinations shows, however, that the listed intensities are in error, and that in reality λ3279 is considerably stronger than λ3073, indicating that $\nu=18581.9$ is an F_3 term and not a D_3. The term $\nu=$ 17901.8 has, therefore, been placed as $^4D'_3$. The line λ3093 shows in the magnetic field as a triplet with separation $(0\pm1.7a)$ and can hardly be other than $m^2D_3-a^4D'_4$.

From the evidence just given, the term $\nu=18581.9$ is very probably a^2F_3 and it has been so designated. Its companion a^2F_4 must then be $\nu=17344.8$, the only remaining term with $j=4$. The doublet separation is 1237.1.

The remaining four terms of the lower term group of Table I should be $^2P_1$ $^2P_2$ $^2D'_2$ $^2D'_3$. The g-value .44 for $\nu=16487.2$ indicates that it can reasonably be called a^2P_1. The Zeeman patterns of λ2824 $(0\pm1.2a)$ and λ2998 $(0\pm1.7a)$ (shaded inwards) agree very well with those calcu-

* Incorrectly given in Kayser and Konen, vol. VII, p. 342 as λ 3293. 903.

lated for $^2D_3-{}^2D'_3$ and $^2D_2-{}^2D'_3$ from Landé's table, i.e. $(0\pm\frac{6}{5}a)$ and $(\pm(13)\,357\overline{9}a)$. This term 15709.7 has, therefore, been designated $a^2D'_3$.

There remain the two terms $\nu=16428.8$ and $\nu=16135.2$ which should be a^2P_2 and $a^2D'_2$. Their g-values are practically identical, and they both combine with m^2D_2 more strongly than with m^2D_3 which is, of course, incorrect for $^2P_2$. It may be that, the spectrum being of the second rank, the identities of these two terms have become confused. With that reservation the term $\nu=16428.8$ has been chosen as a^2P_2 since its combinations with m^2D depart least from the theoretical expectation.

It has been shown that the terms of Table I are in agreement with the predictions of the Hund theory; but that the g-values, as expected, do not agree with those of an ordinary set of quartet and doublet terms. The g-sums should, however, be correct. That is, the sum of the g's of all terms with the same j should equal the sum of the Landé g's for the equivalent quartet and doublet terms. This is correct within the experimental error. The experimental g's are each subject to an error of about .02 for $j=1$ and .04 for $j=2$.

Terms. $j=1$.

g-sum (exp) $2.68+.44+.20=3.32\pm.06$.
g-sum (theor) $\frac{8}{3}+\frac{2}{3}+0=\frac{10}{3}=3.33$.

Terms. $j=2$.

g-sum (exp) $1.10+1.14+1.10+1.70+.44=5.48\pm.20$
g-sum (theor) $\frac{4}{3}+\frac{4}{5}+\frac{6}{5}+\frac{26}{15}+\frac{2}{5}=5.46$

The experimental g-value for a^4F_2 (.44) is from the results of A.R. Loring, who has kindly communicated to me some of his Zeeman effects obtained on the large grating of the Jefferson Laboratory at Harvard University. The value 1.7 for $^4P_2$ is taken from the unresolved pattern given in Table II and may be slightly in error.

Of the remaining terms of Table I, $\nu=12925.0$ is either 3^2P_2 or the pair 3^2P_2 and 3^2P_1 of the ordinary spectrum together. This has been discussed in my previous paper (loc. cit.). The difficulty has not been eliminated by the present investigation.

The eleven terms of Table I which have not yet been considered should include the set of ^2P, D', F, which arise from the addition of a p-electron to the ^1D of the spark. A consideration of intensities of combinations both with m^2D and with the higher terms identifies $b^2F_3=5656.7$ and $b^2F_4=6278.3$ with some certainty. In particular with $c^2G_4=-8819.7$ and $c^2G_5=-8551.3$, they form the intense triplet λ6905 (6), λ6741 (7), λ6621 (4).

Anything approaching a positive identification of the ^2P and $^2D'$ terms is not possible because of the paucity of combination lines. Four terms which may reasonably represent them have been tentatively chosen. The remaining five terms, which should include some members of the quartets arising from the configuration d^8s^2p, have been allotted small letters for identification purposes. The nature of all of these terms could be determined by observations of Zeeman effects in the long wave-length end of the spectrum.

The combinations of 1^2S and m^2D, with the terms of Table I account for almost all of the important lines of the spectrum below λ3100. A large majority of the remaining lines can also be accounted for by the combinations of these terms with a new set of terms, all of which are negative. The starting point for the discovery of these negative terms was given by the constant frequency differences of Rydberg.[10] Two of these differences occur as $a^4D'_4 - a^2F_3 = 212.2$ and $a^2F_3 - a^4D'_3 = 680.1$. The other two 50.4 and 129.7 are differences of negative terms.

The origin of the negative terms must be sought in electron configurations from which transitions can take place to the structure d^9sp. Such a one is d^9ss mentioned above, which can be responsible for $^4D_1$ ^2D and ^2D. From analogy with the spectra of the preceding elements iron, cobalt and nickel, the ^4D term should be the lowest and should produce strong multiplets in combination with a^4P, a^4D' and a^4F of the Table I. Such a quartet term is found in the following three multiplets (Table III).

TABLE III
Multiplets

		c^4D_4 −95.2	c^4D_3 −640.2	c^4D_2 −1276.4	c^4D_1 −2164.2
a^4P_3	23289.4	(6) 23384.5	(4u) 23929.6	24565.8 (calc)	
a^4P_2	22194.0		(6u) 22834.0	(2u) 23470.7	(2) 24358.2
a^4P_1	21364.3			(3u) 22640.6	(4) 23528.5
a^4F_5	21398.9..	(8) 21494.2			
a^4F_4	21154.6	(6) 21249.9	(6u) 21794.8		
a^4F_3	20745.2	(2) 20840.4	(6u) 21385.5	(4u) 22021.7	
a^4F_2	20005.6		(1u) 20646.0	(4u) 21282.0	(4) 22169.8

[10] Rydberg, Astrophys. J. **6**, 239 (1897).

TABLE III (continued)

		c^4D_4 −95.2	c^4D_3 =640.2	c^4D_2 −1276.4	c^4D_1 −2164.2
a^4D_4'	18794.1	(4) 18889.3	(1*u*) 19434.3		
a^4D_3'	17901.8	(3) 17997.0	(2*u*) 18542.0	(1*u*) 19177.9	
a^4D_2'	17763.9		(2*u*) 18404.2	(1*u*) 19040.5	(3) 19928.1
a^4D_1'	17392.3			(1*u*) 18669.0	(2) 19556.6

The identities of the terms designated c^4D_1 and c^4D_2 in these multiplets are fixed beyond doubt by the results of Loring at Harvard University. The g's of these two terms are 0 and $\frac{10}{7}$ the theoretical values given by Landé. The two other terms have the distinct peculiarity that all their lines are diffuse lines. Moreover, the sharp lines due to c^4D_1 and c^4D_4 are much more sensitive to low voltage discharge. In spite of such differences in behaviour, however, there can be little doubt that the four terms do form a complete ^4D term; and in all probability it is the one mentioned above arising from d^9ss. Confirmation of the identity of c^4D_2 is obtained from Loring's unresolved Zeeman pattern for λ4587, $a^4F_4-c^4D_3$. In the magnetic field the line shows as a triplet (0).97*a*. The theoretically strongest component would be the innermost at .9*a*. None of the other lines arising from c^4D_2 or c^4D_3 appear as anything but a wide haze.

It has not, as yet, been found possible to designate all of the negative terms. This arises from several causes. First, there are so many possibilities involved in the structures in which these terms have their origin. The possible terms originating in d^9ss mentioned above are probably mingled not only with d^9sd but also with d^8s^2d. Such configurations produce a multitude of quartet and doublet terms of all types from S to H. Moreover, term separations will certainly be large, and will not necessarily decrease as we proceed to higher series members since the limits may be different components of the spark ^3D and ^1D. The intensities given in the table are not sufficiently accurate nor on a large enough scale to be of much value. A thorough investigation of relative intensities is, perhaps, the best method of attack on these negative terms.

Table IV contains all of the negative terms. Where no notation has been assigned, the terms are given in small letters using as subscript the most probable j value. The last column contains the number of combinations made with the terms of Table I.

TABLE IV

Term	j	Intervals		Designation.	No. of Comb.
−95.2	4			c^4D_4	9
		545.0			
−640.2	3			c^4D_3	10
		636.2			
−1276.4	2			c^4D_2	8
		887.8			
−2164.2	1			c^4D_1	7
−2349.5	3			c^2D_3	9
−4834.3	3			a_3	5
−5663.9	2			b_2	6
−8545.3	2			d^4S_2	11
−8551.5	5			c^2G_5	5
−8690.0	3 or 4	268.2		c_2	6
−8790.2	3			d_2	12
−8819.7	4			c^2G_4	10
−8822.6	6	848.1		d^4G_6	1
−8870.1	3			d^4P_3'	13
−8960.1	4			d^4D_4	8
		749.0			
−8982.4	5			d^4F_5'	6
−9574.9	1			d^4P_1'	6
		−44.2			
−9619.1	2		798.8	d^4P_2'	10
		802.6			
−9670.7	5			d^4G_5	5
		37.9			
−9708.6	4			d^4G_4	8
−9758.9	3			d^4D_3	13
		134.5			
−9785.0	4			d^4F_4'	11
−9843.1	2 or 3			d^4G_3	
−10794.6	3 or 4			g_4	4
		1211.5			9
−10796.8	1			c^2S_1	8
−10890.7	2 or 3			h_2	9
−10996.5	2 or 3			d^4F_3'	10
		11.9			
−11008.4	2			d^4F_2'	8
−11687.0	4			e^4D_4	4
		317.6			
−12004.6	3			e^4D_3	5
−12801.3?	1	970.9		1_1	3
−12955.4	2	780.9		c^2P_2'	5
−12975.5	2			e^4D_2	3
−13264.8?	3 or 4			n_4	3
−13756.4	1			e^4D_1	4
−14722.0?	3 or 4			o_4	3
−14760.1?	3 or 4			p_4	3
−14772.4?	3 or 4			q_4	3

Fig. 1 gives the intensities of all the lines produced by combination of the positive and negative terms. The intensity of a line appears opposite the two terms whose difference is the frequency of the line.

On the basis of the somewhat unreliable available data, a number of negative terms may be identified with reasonable certainty. The combinations of the pair of terms b^2G mentioned above agree very well with

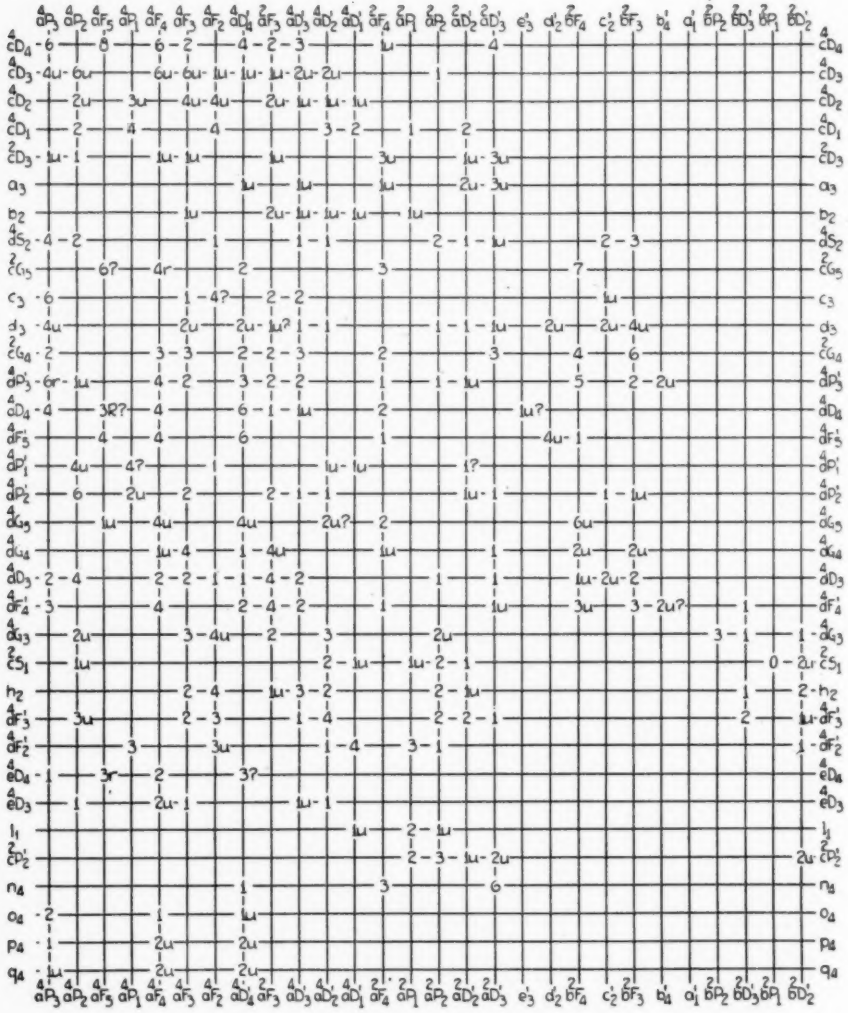


Fig. 1. Diagram giving the intensities of all the lines produced by combination of the positive and negative terms.*

those that would be expected theoretically. The identification of the four terms of Table IV listed as a complete $^4F'$ term is based on the following incomplete multiplets. Intensities only are given.

* The terms d^4G_8, g_4, e^4D_2, e^4D_1 of Table IV are omitted in Fig. 1, having been found after the plate had been made.

		$^4D'$				^4F				^4P		
		4	3	2	1	5	4	3	2	3	2	1
$^4F'$	5	(6)				(4)	(4)					
	4	(2)	(2)				(4)			(3)		
	3		(1)	(4)				(2)	(3)		(3u)	
	2			(1)	(4)				(3u)			(3)

The term separations are 11.9 : 1211.5 : 802.6. These are not unreasonable when the proximity of the limit is considered as well as the probability that the $^4F_2$ and $^4F_3$ terms converge to a single member of the spark ^3D, whereas $^4F_4$ and $^4F_5$ will converge to the other two members whose separations should be large.

A partially inverted $^4P'$ term is listed in Table IV. The combinations with the $^4D'$, ^4F and ^4P of Table I are as follows:—

		$^4D'$				^4F				^4P		
		4	3	2	1	5	4	3	2	3	2	1
$^4P'$	3	(3)	(2)				(4)	(2)		(6r)	(1u)	
	2		(1)	(1)				(2)			(6)	(2u)
	1			(1u)	(1u)				(1)		(4u)	(4)?

In addition to the above $^4F'$ and ^4P terms, a $^4S_2$ and parts of a ^4G and ^4D term have been identified. If the strong line λ3307.952 (8) is taken as a $^4F_5 - d^4G_6$, the term $d^4G_6 = -8822.6$; and the $F\ G$ and $D\ G$ multiplets are:—

		a^4F				a^4D'			
		5	4	3	2	4	3	2	1
d^4G	6	(8)							
848.1									
	5	(1u)	(4u)			(4u)			
37.9									
	4		(1u)	(4)	(3)	(1)	(4u)		
134.5									
	3				(4u)			(3)	

The intensities of combinations given by the terms g_4 and h_2 of Table IV would allow them also to be classified as $^4G_4$ and $^4G_3$. Moreover, the intervals would then be more in agreement with those of the term ^4F. The choice between these alternatives must be left for decision on the basis of more certain evidence.

The set of terms ^4S, P', D, F' G which have just been considered are probably those which theoretically result from the addition of a d-electron

to the positive ion configuration d^9s; such terms would be expected, as is observed, to combine strongly with the configuration d^9sp, the terms of Table I. A part of another ^4D term is also given in Table IV. It is dealt with below in connection with limits.

Confirmation of the nature of a number of the terms just considered is given by the following unresolved Zeeman patterns. Of the calculated Zeeman patterns, only the theoretically strongest components are given.

λ	Z.E. (obs)	Z.E. (calc)	Comb.
3290.55	(0)1.31	(0)1.33	a^4F_5—d^4F_5'
3231.17	(0)1.24	(0)1.24	a^4F_4—d^4F_4'
3224.65	(0)1.94	(−)−1.98	a^4F_2—d^4F_3'
3223.43	(0)0+	(0) .4	a^4F_2—d^4F_2'
3099.92	(0)1.03	(−) .97−	a^4P_3—d^4D_4
3128.69	(0) .95	(−) .84−	a^4P_2—d^4D_3
3108.60	(0)1.52	(0)1.6	a^4P_3—d^4P_2'
3243.16	(0) .96	(−) .97−	a^4F_4—d^4G_5
3335.24	(0)1.16	(−)−1.06	a^4F_4—c^2G_4
3307.95	(0)1.11	(−)1.0−	a^4F_5—d^4G_6

(The last line is from Loring's results).

The remaining terms of Table IV should in the main belong to the doublet system but three only have been designated with any certainty. These are a $^2P_2$, a ^2S, and a $^2D_3$. The line intensities are low and the combinations few. A number of the terms given are calculated from only three combinations and are, therefore, perhaps doubtful. The three highest terms o_4, p_4 and q_4 are peculiar in the similarity of their combinations and in the fact that they include three lines which appear in the low voltage arc. The difference o_4-q_4 is 50.4, one of Rydberg's[11] differences. It occurs also in two other places as the difference of two negative terms.

It has been mentioned above that the terms m^2D should be the leading members of two series, one of which should converge to the spark ^1D (d^9s). The other should have as its two limits two of the three ^3D spark terms. It is of the greatest importance to find the higher members of these two series. O. Laporte has kindly communicated to me a conclusion to which he has come from the consideration of other complicated spectra; namely, that the following inequality of terms should be true.

$$\left\{(d^{s-2}s^2)-(d^{s-1}s)\right\}\text{ arc} > \left\{(d^{s-2}s)-(d^{s-1})\right\}\text{ spark}$$

In the case of the copper spectrum this means that the total length of the series headed by m^2D should be greater than the length of the ^2S series. Since $1^2S-m^2D=11202.5$, the limit of the ^2D series must be higher than -11202.5. The second member of the ^2D series (d^9ss) should be looked

[11] Rydberg, Astrophys. J. **6**, 239 (1897).

for in the neighborhood of c^4D which is also presumably due to d^9ss. A term which gives combinations of the correct relative intensities is found at -2349.5. Taking this as the second member, the series limit is calculated to be about -24000. Confirmation* of such a value for the limit is obtained by considering the terms c^4D and e^4D as successive members of the series of quartet terms which are also due to d^9ss. The calculated limits fall at about -22300, in sufficient agreement with the limit calculated above from the ^2D terms. This means that the difference between the ^1S and ^3D of the spark spectrum is about 22300 cm^{-1}, the ^1S being the lower. The justification for the calculation of even approximate series limits from only two terms is contained in the fact, communicated to me by Laporte, that, in complicated spectra, series of terms which are due to the change in total quantum number of an s-electron only, are very closely "Rydbergian."

The behaviour of the spectrum lines in various sources is peculiar. The author made, some time ago, a large number of observations on the spectrum emitted by a low voltage arc in copper vapour. Excitation by six to seven volt electrons produces only the lines involving ^2S and m^2D and 2^2P. An arc at about eight volts and low current brings out a number of other lines, but by no means in the order in which the ordinary arc intensities would lead one to expect. Instead, the lines emitted practically all belong to four of the negative terms: namely, $c^4D_4 = -95.2$, $c^4D_1 = -2164.2$, and the terms $c^2G_4 = -8819.7$, $d^4D_4 = -8960.1$. Each of three other terms include in their combinations two low voltage arc lines, namely, $c^2G_5 = -8551.5$, $e^4D_4 = -11687.0$ and $q_4 = -14772.4$. The lines in question remain the only arc lines emitted even when the potential in the arc is sufficient to excite many of the ultra-violet spark lines. This peculiar behaviour is paralleled by the observations of R. S. Mulliken[12] on the excitation of copper lines by the action of active nitrogen on the copper halides. The same lines were observed in that experiment together with a number of new lines which are considered in connection with the regular doublet spectrum.

Ordinary Series

Since it has been found possible to add several terms to the ordinary doublet series of copper, it seems useful to restate the details of that part of the spectrum. The values of $1^2S = 62308.0$, and of the other known terms, are taken from Fowler's[1] calculations of the diffuse and sharp

* The discovery by the author since this paper was written that the extreme interval of the lowest spark ^3D (d^9s) is almost exactly equal to c^4D_4–c^4D_1 and e^4D_4–e^4D_1 is excellent confirmation of the correctness of the assignation of these terms to the structure d^9ss.

[12] R. S. Mulliken, Phys. Rev. **26**, 1 (1925).

TABLE V

Principal Series. $1^2S_1 - n^2P$.

$1^2S_1 = 62308.0$

λ		ν	Δν	n	$n^2P_{1,2}$
3273.967	(10r)	30535.2	248.4	2	31772.8
3247.550	(10r)	30783.6			31524.4
2024.33	(R)	49383.0	0 ?	3	12925.0

series. The terms added agree so well with those calculated that no alteration in the limit is necessary. The principal series (Table V) is represented by the resonance lines and by one strong reversed line in the proper position for $1^2S - 3^2P_2$. As mentioned above this term 3^2P_2 is apparently single.

It has been found possible to extend the sharp series (Table VI) to the term 6^2S by including the pairs λ3598.01 (2*u*), λ3566.14 (1*u*) and λ3463.5 (1*u*), λ3433.98 (1) Ex. The terms $5^2S = 3739.2$ and $6^2S = 2660.3$ fit very well into the series as given by Fowler.

TABLE VI

Sharp Series. $^2P_{2,1} - nS$

$^2P_1 = 31772.8$ $^2P_2 = 31524.4$

λ		ν	Δν	n	n^2S
8092.74	(10)	12353.4	248.4	2	19171.1
7933.20	(10)	12601.8			
4530.843	(6r)	22064.8	248.5	3	9459.5
4480.376	(6r)	22313.3			
3861.755	(3u)	25887.7	248.4	4	5636.7
3825.05	(3)	26136.1			
3598.01	(2u)	27785.3	248.3	5	3739.2
3566.14	(1u)	28033.6			
3463.5	(1u)	28864.3	248.1	6	2660.3
3433.98	(1) Ex.	29112.4			

Three new members and a possible fourth have been added to the diffuse series. The lines λ3512.122 (4*u*) and λ3481.9 (1*u*) are $2^2P_2 - 6^2D_3$ and $2^2P_1 - 6^2D_2$. The disparity between the intensities is accounted for by the fact that λ3512 is, undoubtedly, at least one other combination. It

may in reality be three lines, since $^2P_2 - 6^2F$ also falls in this position. The further extension of this series is made possible by Mulliken's experiments mentioned above. In his experiments a number of new lines were measured and attributed to copper. Several of them have also been observed by the author in the low-voltage arc. It now appears that these lines are mainly, at least, members of the diffuse series. The wave-length measurements are at best accurate to .1°A, but they agree very reasonably with the calculated positions of the higher series members. In Table VII the values of the terms 7, 8, 9*D* have been obtained by extrapolation from the known terms and not from the observed lines.

TABLE VII

Diffuse Series. $2^2P_{2,1} - n^2D_{2,3}$.
$2^2P_1 = 31772.8$ $2^2P_2 = 31524.4$

λ		ν	Δν	n	$n^2D_{2,3}$.
5220.041	(6)	19151.6		3	12372.8
			6.9		
5218.170	(10)	19158.5	248.3		12365.9
5153.226	(8*u*)	19399.9			
4063.296	(4*u*)	24603.6		4	6920.8
			3.7		
4062.694	(6*u*)	24607.3	248.5		6917.1
4022.667	(6*u*)	24852.1			
3687.5	(3*u*)	27111.0		5	4415.5
3654.3	(2*u*)	27357.3			4413.4
3512.122	(4*u*)	28464.7		6	3059.7
3481.9	(1*u*)	28711.8			3061.0
					Calc. from series.
3414.2	(Mul)	29281.1		7	2245.0
3385.4	(Shen)	29530.2			
3353.8	(Mul)	29808.4		8	1718.
3326.2	(Mul)	30055.7			
3313.2	(Mul)	30174.0		9	1357. ?

The first pair of lines only of the fundamental series is known (Table VIII), but the *F* terms may be calculated from combinations with m^2D and 2^2P (Table IX). If these combinations are assumed correct, it appears

TABLE VIII

F—series. $3^2D_2 = 12372.8$; $3^2D_3 = 12365.9$.

λ	ν	n	$nF_{3,4}$.
18229.5	5484.1	4	6880.0
18194.7	94.6	5	4400.0
		6	3059.0

that the approximate values of the 4^2F term are $4^2F_3 = 6879.1$ and $4^2F_4 = 6881.6$. The term would, therefore, be inverted, which would be strange

TABLE IX

Combinations

λ	Int.	ν (obs.)	ν (calc.)	Comb.
16008.5		6245.0	6246.1	2^2S—3^2P_2
16653.4		6003.2	6004.2	3^2P_2—4^2D_3
5782.158	(8)	17289.8	17289.8	m^2D_2—2^2P_1
5700.249	(6)	17538.2	17538.2	m^2D_2—2^2P_2
5105.55	(8*u*)	19581.1	19581.1	m^2D_3—2^2P_2
2766.39	(8)	36137.6	36137.6	m^2D_2—3^2P_2
2618.38	(10*r*)	38180.2	38180.5	m^2D_3—3^2P_2
2369.89	(6)[a]	42183.1	42182.6	m^2D_2—4^2F
2260.51	(4)	44224.1	44225.5	m^2D_3—4^2F
2238.45	(2*u*)	44659.9	44662.6	m^2D_3—5^2F
4056.7	(2*Rv*)	24643.6	24644.4	2^2P_2—4^2F
4015.8	(1*u*)	24894.6	24892.8	2^2P_1—4^2F?
3652.40	(1*u*)	27371.5	27372.8	2^2P_1—5^2F?

[a] Also a spark line.

in a spectrum of this type. The peculiar PF combinations have been included although they involve violations of both the k and j selection principles. The theoretical and experimental frequencies do not agree very closely.

It is of importance to note that none of the terms of this normal spectrum, except ^2S, combine with any of the terms of the complicated spectrum, although this could not be predicted from the assumed atomic structures. For instance, there is nothing theoretically to prevent a transition from $d^{10}d$ to d^9sp, but it apparently does not occur.

The present analysis of the copper arc spectrum is in almost total disagreement with that given by H. Stücklen[13] in a recent paper. The analysis given in that paper is based on experiments with the under-water spark between copper electrodes. A number of lines are arranged in groups according to their appearance in absorption as the self-induction of the circuit is changed. The lines obtained by this method are arranged in six groups and are presumed to be all arc lines. The last three groups, however, contain spark lines. From the conditions of excitation, there cannot be much doubt that these spark lines are from low terms of the spark system. The lines in question are λ2192.24, 2246.98, 2242.60, 2218.08. 2210.24, 2189.60. In the analysis they are considered as arc lines

[13] H. Stücklen, Zeits. f. Physik. **34**, 562 (1925).

and some of them are included in two multiplets together with lines which are certainly arc. There can be no doubt that the arrangement in the form of multiplets is merely fortuitous. Amongst other constant frequency differences given in Stücklen's paper is 1497.9. This difference actually occurs no less than eight times and always between spark lines. The Zeeman effect of one of the pairs of lines is as follows:—

	Z.E. (obs.)	(calc.)	Desig.
2356.623	± (0,.9)1.45, $\overline{2.49}$	$\frac{\pm(0\ 2)1,3,5}{2}$	$^3D_1-{}^3P_2$
2276.261	± (1.0) .48, 1.52	$\frac{\pm(2)1,\ 3}{2}$	$^3D_1-{}^3P_1$

It seems probable that the $^3D_1$ term involved is the low spark ^3D which is due to the configuration d^9s. A considerable number of other regularities in the spark spectrum have been found and an analysis is being attempted.* It is important to find the ^1S term (d^{10}) but it seems likely from the calculation of arc limits that its value is so low that the lines due to its combinations will be found to lie well outside of the quartz region.

The copper arc spectrum has been shown to be in agreement with the Heisenburg-Hund theory. The structure may be represented by the diagram of Fig. 2. The negative energies in wave-numbers are given on the left hand side. The zero of energy is the ^1S spark term, the other spark terms then assuming negative values.

A few only of the terms of the ordinary arc series are given on the left of ^2S, and heavy arrows are used to denote their inter-combinations. Dotted arrows indicate the limit of the particular series of terms when the total quantum number becomes large. On the right are the terms of the complicated spectrum founded on m^2D. They are grouped in the sets which arise from the particular electron configurations which are given in brackets. The few known terms which are probably due to the configurations d^8s^2p and d^8s^2d are omitted. They would have as limits the spark terms $^1S{}^1D{}^1G{}^3P{}^3F$, all of which will probably be higher than ^1D.

The selection rule for the possible transitions from one configuration to another is, as given by Heisenberg,[4]

* The spark spectrum has now been analysed. The strong lines are almost all due to the combinations of a low ^3D and ^1D and a high ^3D and ^1D (d^9s) with an intermediate triad ^3P, D', F, ^1P, D', F (d^9p) The combinations of the last named terms with ^1S (d^{10}) would lie outside the observed region of the spectrum.

change in $k_1 = \pm 1$
change in $k_2 = 0, \pm 2$

where k_1 and k_2 are the azimuthal quantum numbers of the two electrons involved. No violations of this rule have been found within the second

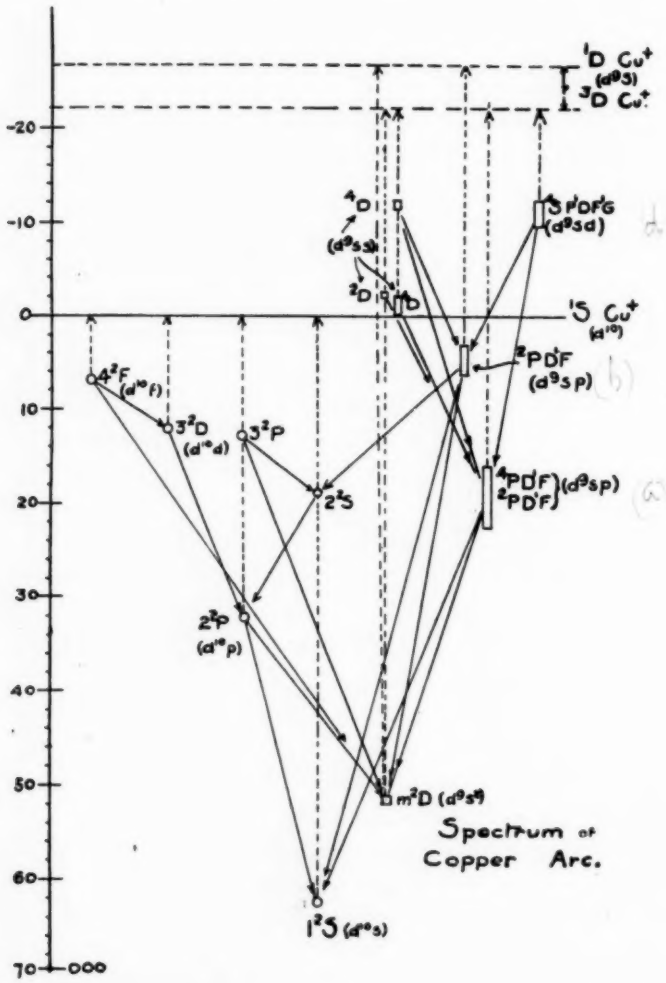


Fig. 2. Term diagram of the copper arc spectrum. Groups of terms, only, are indicated, and the electron configuration is given in brackets after each group. Dotted lines indicate limits and full lines, combinations.

rank part of the spectrum; but there are, apparently, violations in the combinations which occur between 2^2P ($d^{10}p$) and ^2F ($d^{10}f$) of the ordinary spectrum, and also in the combinations of m^2D (d^9s^2) with ^2F ($d^{10}f$). In the

latter case $\Delta k_1 = 3$ and $\Delta k_2 = 2$. There seems, however, to be another restricting influence which prevents transitions from the ordinary to the heavy metal types of electron configuration, except for the particular cases of $d^{10}s$ and d^9s^2. For instance, it might be expected that 2^2P ($d^{10}p$) would produce strong lines in combination with members of the d^9ss and d^9sd sequences, but no such combination lines can be found. The lack of the transition $d^9ss \rightarrow d^{10}p$ is particularly strange when one considers the strength of the known triplet $m^2D - 2^2P$ ($d^{10}p \rightarrow d^9s^2$). The relative intensity of these two combinations should be comparable to that of the first members of the principal and sharp series.

Table X contains the wave-lengths of all the lines of the copper arc spectrum which have been classified. The wave-lengths used are mainly those given by Meggers and by Hasbach. The gap between their observation is filled by the measurements of Aretz; and, over the whole spectrum, faint lines measured by other observers have been included. The allow-

TABLE X

Wave-lengths of all the classified lines of the copper arc spectrum.

λ	Authority	Intensity	ν	Designation.	ν(calc) − ν(obs)
18229.	R	5	5484.1	$3^2D_3 - 5^2F_4$	1.8
194.	R	7	5494.6	$3^2D_2 - 5^2F_3$	−1.8
16653.	R	4	6003.2	$3^2P_2 - 4^2D_2$	1.0
008.	R	5	6245.0	$2^2S - 3^2P_2$	1.1
8092.74	M	10	12353.4	$2^2P_2 - 2^2S$	
7933.20	M	10	12601.8	$2^2P_1 - 2^2S$	
7570.09	M	5	13206.3	$2^2S_1 - c_2'$	
7427.26	M	1	13460.2	$b^2D_2' - d^4G_3$	.1
7193.56	M	2u	13897.5	$b_4' - d^4P_3'$	− .1
54.29	M	1	13973.8	$b^2D_3' - d^4F_4'$	− .1
24.66	M	1	14031.9	$b^2D_2' - d^4G_3$	− .1
7039.34	M	3	14202.0	$b^2F_3 - d^4S_2$ $b^2P_2 - d^4G_3$	− .1
00.02	M	1u	14281.7	$2^2S - a_1'$	
6935.80	M	2u	14414.0	$b^2D_2' - c^2S_1$	
20.09	M	4u	14446.7	$b^2F_3 - d_3$	.2
05.90	M	6	14476.4	$b^2F_3 - c^2G_4$	
6890.90	M	2	14507.9	$b^2D_2' - h_2$	
89.92	M	2	14510.0	$c_2' - d^4S_2$	
81.94	M	2	14526.8	$b^2F_3 - d^4P_2'$	
40.99	M	1u	14613.7	$b^2D_2' - d^4F_3'$	
35.46	M	1	14625.6	$b^2D_2' - d^4F_2'$	
21.86	M	1u	14654.7	$c_2' - c_3$	
6781.90	A	0	14741.1	$b^2P_1 - c^2S_1$	
75.64	M	2u	14754.7	$c_2' - d_3$	.2
49.29	M	2u	14812.3	$b_4' - d^4F_4'$ $2^2S_1 - b^2P_2$	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation.	ν(calc) − ν(obs)
6741.42	M	7	14829.6	b^2F_4—c^2G_5	.2
6672.23	M	3	14983.4	b^2D_3'—g_4	− .1
29.67	M	1	15079.6	b^2D_3'—h_2	− .2
21.61	M	4	15097.9	b^2F_4—c^2G_4	.1
6599.68	A	5	15148.1	b^2F_4—d^4P_3'	.3
83.54	A	2	15185.2	b^2D_2'—d^4F_2'	
65.54	M	3*u*	15226.8	2^2S_1—b^2P_1	
50.98	M	1	15260.7	b^2F_4—d^4F_5'	
44.51	M	1*u*	15275.8	b^2F_3—d^4P_2'	
06.14	A	2*u*	15365.9	b^2F_3—d^4G_4	− .6
6485.18	M	2	15415.5	b^2F_3—d^4D_3	.1
74.20	M	3	15441.7	b^2F_3—d^4F_4'	
27.57	M	1	15553.7	2^2S_1—b^2D_2'	.2
15.18	A	1	15583.7	c_2'—d^4P_2'	.1
6358.09	A	2*u*	15723.7	c_2'—d^4D_3	− .1
25.45	A	4	15804.8	a^2D_3—c^4D_4	.1
6292.86	A	2	15886.6	a_1' —d^4F_3' ?	− .7
68.30	A	6*u*	15948.9	b^2F_4—d^4G_5 b^2P_1—c^4D_3 ?	.1
53.37	A	2*u*	15987.0	b^2F_4—d^4G_4	− .1
33.79	A	1*u*	16037.2	b^2F_4—d^4D_3	
23.66	A	3*u*	16063.3	b^2F_4 —d^4F_4'	
20.94	A	2*u*	16070.3	d_2'—d_2	.2
6147.31	A	4*u*	16262.8	d_2'—d^4F_5'	
27.73	A	2*u*	16314.8	e_3'—d_3 ?	− .7
6064.69	A	1*u*	16484.3	e_3'—d^4D_4	− .3
32.33	A	2*u*	16572.8	b^2D_2'—c^2P_2'	− .2
5857.03	Ed.	1	17068.8	a^2P_2—c^4D_3	.2
5782.158	H	8	17289.8	m^2D_2—2^2P_1	
32.36	H	1*u*	17440.0	a^2F_4—c^4D_4	
00.249	H	6	17538.2	m^2D_2—2^2P_2	
5554.94	H	3	17997.0	a^4D_3'—c^4D_4	
35.78	H	3*u*	18059.3	a^2D_3'—c^2D_3	− .1
5462.97	Ed.	2	18300.0	a^2D_3'—c^4D_1	− .6
32.05	H	2*u*	18404.2	a^4D_2'—c^4D_3	− .1
08.46	H	1*u*	18484.4	a^2D_2'—c^2D_2	.3
5391.67	H	2*u*	18542.0	a^4D_3'—c^4D_3	
60.045	H	1	18651.4	a^2P_1—c^4D_1	
55.0	H	1*u*	18669.0	a^4D_1'—c^4D_2	− .3
52.68	H	2	18677.1	a^2F_3—c^4D_4	
5292.539	H	4	18889.3	a^4D_4'—c^4D_4	
50.5	Ex.	1*u*	19040.5	a^4D_3'—c^4D_2	− .2
20.041	H	6	19151.6	2^2P_2—3^2D_2	
18.170	H	10	19158.5	2^2P_2—3^2D_3	
12.89	A	1*u*	19177.9	a^4D_3'—c^4D_2	.2
00.87	H	1*u*	19222.2	a^2F_3—c^4D_3	− .1
5153.226	H	8*u*	19399.9	2^2P_1—3^2D_2	.1
44.12	H	1*u*	19434.3	a^4D_4'—c^4D_3	
11.945	H	2	19556.6	a^4D_1'—c^4D_1	− .1
05.551	H	8*u*	19581.1	m^2D_3—2^2P_2	
5076.2	H	3*u*	19694.3	a^2F_4—c^2D_3	
34.3	H	2*u*	19858.2	a^2F_3—c^4D_2	.1
16.634	H	3	19928.1	a^4D_2'—c^4D_1	
4866.4	H	3*u*	20543.4	a^2D_2'—a_3	.6
42.2	Ex.	1*u*	20646.0	a^4F_2—c^4D_3	− .2
4797.042	H	2	20840.4	a^4F_3—c^4D_4	
76.2	H	1*u*	20931.3	a^2F_3—c^2D_3	.1
67.5	H	2*u*	20969.5	a^2D_2'—a_3	
04.598	H	6	21249.9	a^4F_4—c^4D_4	− .1
4697.49	H	4*u*	21282.0	a^4F_2 —c^4D_2	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs.)
4674.76	H	6*u*	21385.5	a^4F_3—c^4D_3	− .1
51.13	H	8	21494.2	a^4F_5—c^4D_4	− .1
4586.97	H	6*u*	21794.8	a^4F_4—c^4D_3	
39.70	H	4*u*	22021.7	a^4F_3—c^4D_2	− .1
30.843	H	6*r*	22064.8	2^3P_2—3^3S	.1
13.20	H	1*u*	22151.0	a^2P_1—b_2	.1
09.386	H	4	22169.8	a^4F_3—c^4D_1	
07.5	H	1*u*	22179.0	a^2F_4—a_3	.1
4480.376	H	6*r*	22313.3	2^3P_1—3^3S	
15.60	H	3*u*	22640.6	a^4P_1—c^4D_2	.1
4397.0	Ex.	1*u*	22736.4	a^4D_3'—a_3	− .3
78.2	H	6*u*	22834.0	a^4P_2—c^4D_3	.2
36.0	Ex.	1*u*	23056.3	a^4D_1'—b^2	− .1
− 28.7	Ex.	1*u*	23095.2	a^4F_3—c^2D_3	− .5
4275.131	H	6	23384.5	a^4P_2—c^4D_4	.1
67.2	Ex.	1*u*	23428.0	a^4D_2'—b_2	− .1
59.43	H	2*u*	23470.7	a^4P_2—c^4D_2	− .3
53.34	Ex.	1*u*	23504.3	a^4F_4—c^2D_3	− .2
—48.969	H	4	23528.5	a^4P_1—c^4D_1	
42.26	H	1*u*	23565.7	a^4D_3'—b_2	
− 31.0	Ex.	1*u*	23628.4	a^4D_4'—a_3	
4177.758	H	4*u*	23929.6	a^4P_2—c^4D_3	
23.27	H	2*u*	24245.8	a^2F_3—b_3	
21.7	H	1*u*	24255.0	a^2D_3'—d^4S_2	
04.233	H	2	24358.2	a^4P_2—c^4D_1	
4080.534	H	1*u*	24499.7	a^2D_3'—d_3	.2
75.592	H	3	24529.4	a^2D_3'—c^2G_4	
73.27	Ex.	1	24543.4	a^4P_2—c^2D_3	.1
63.296	H	4*u*	24603.6	2^3P_2—4^3D_3	
62.694	H	6*u*	24607.3	2^3P_2—4^3D_2	
56.7	H	2*Rv*	24643.6	2^3P_2—4^3F	.8
50.656	H	1	24680.4	a^2D_2'—d^4S_2	.1
22.667	H	6*u*	24852.1	2^3P_1—4^3D_2	− .1
4015.8	H	1*u*	24894.6	2^3P_1—4^3F_3	−1.8
10.85	Ex.	1	24925.4	a^2D_2'—d_3	
03.038	H	2	24974.0	a^2P_2—d^4S_2	.1
3997.93	C.T.	1*u*	25005.9	a^2D_2'—d^4P_3'	− .6
64.15	Ex.	1	25219.0	a^2P_2—d_3	
51.48	C.T.	1	25299.8	a^2P_2—d^4P_3'	− .9
46.88	Ex.	1	25329.3	a^2D_3'—d^4P_2'	− .5
33.00	Ex.	1	25418.7	a^2D_3'—d^4G_4	− .4
25.274	H	1	25468.7	a^2D_3'—d^4D_3	− .1
21.274	H	1*u*	25494.7	a^2D_3'—d^4F_4'	
3899.1	Ex.	1*u*	25639.7	a^4P_2—c^2D_3 ?	− .8
88.58	C.T.	1	25709.1	a^2D_2'—d^4P' ?	1.0
81.71	Ex.	1*u*	25754.6	a^2D_2'—d^4P_2'	− .3
62.75	Ex.	1	25881.0	3^3P_2—c^2P_2' ?	− .6
61.755	H	3*u*	25887.7	2^3P_2—4^3S	
60.467	H	3	25896.3	a^2F_4—c^2G_5	
25.050	H	3	26136.1	2^3P_1—4^3S	
20.879	H	2	26164.6	a^2F_4—c^2G_4	− .1
17.50	H	1	26187.8	a^2P_2—d^4D_3	− .1
13.54	H	1	26214.9	a^2F_4—d^4P_3'	
05.30	H	2*u*	26271.7	a^2P_2—d^4G_3	.2
00.499	H	2	26304.9	a^2F_4—d^4D_4	
3799.88	H	1	26309.2	a^4D_2'—d^4S_2	
97.19	C.T.	1	26327.7	a^2F_4—d^4F_5'	− .5
85.60	C.T.	1*u*	26408.4	a^4F_5—b_3	.7
80.05	Ex.	1	26447.2	a^4D_3'—d^4S_2	− .1
71.902	*H*	2	26504.3	a^2D_3'—g_4	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs)
3764.82	Ex.	1	26554.2	a^4D_2'—d_3	− .1
59.495	H	2	26591.8	a^4D_3'—c_3	
45.38	C.T.	1	26692.0	a^4D_3'—d_3	
43.38	C.T.	1	26706.4	a^2D_2'—d^4F_3'	− .2
− 41.247	H	3	26721.5	a^4D_3'—c^2G_4	
34.23	H	2	26771.7	a^4D_2'—d^4P_2'	.1
3721.70	H	1*u*	26861.8	a^4D_3'—d^4D_4	
20.770	H	2	26868.5	m^2D_2—a^4P_2	.1
12.00	H	1	26932.0	a^2D_2'—c^2S_1	
07.16	C.T.	1*u*	26967.2	a^4D_1'—d^4P_1'	
00.532	H	2	27015.5	a^2F_4—d^4G_5	
3699.1	H	1*u*	27025.9	a^2D_2'—h_2	
95.33	C.T.	1*u*	27053.5	a^2F_4—d^4G_4	− .1
87.5	H	3*u*	27111.0	2^2P_2—5^2D_3	
84.925	H	1	27129.9	a^2F_4—d^4F_4'	− .1
84.671	H	2	27131.8	a^2D_2'—d^4F_3'	− .1
71.969	H	2	27225.6	a^2P_2—c^2S_1	
65.740	H	2	27271.9	a^2F_3—c_3	
64.06	C.T.	1*u*	27284.4	a^2P_1—c^2S_1	− .4
59.358	H	2	27319.4	a^2P_2—h_2	.1
56.787	H	1*u*	27338.7	a^4D_3'—d^4P_1'	.1
55.865	H	2	27345.6	a^4D_4'—c^2G_5	
54.3	H	2*u*	27357.3	2^2P_1—5^2D_2	
52.40	H	1*u*	27371.5	2^2P_1—5^2F ? a^2F_3—d_3	1.3 .6
50.864	H	1	27383.0	a^4D_2'—d^4P_2'	
48.385	H	2	27401.6	a^2F_3—c^2G_4	
45.236	H	2	27425.3	a^2P_2—d^4F_3'	
44.05	K	2*u*	27434.2	a^4D_2'—d^4G_5 ?	.4
43.65	C.T.	1	27437.2	a^2P_2—d^4F_2'	
41.693	H	2	27452.0	a^2F_3—d^4P_3'	
35.923	H	3	27495.5	a^2P_1—d^4F_2'	.1
32.56	H	1	27521.0	a^4D_3'—d^4P_2'	− .1
29.794	H	1	27541.9	a^2F_3—d^4D_4	.1
24.236	H	2*u*	27584.2	a^4D_4'—d_3	.1
21.248	H	3	27607.0	a^4D_2'—d^4G_3	
20.346	H	2	27613.8	a^4D_4'—c^2G_4	
14.216	H	2	27660.7	a^4D_3'—d^4D_3	
3613.755	H	3	27664.2	a^4D_4'—d^4P_3'	
10.806	H	2	27686.8	a^4D_3'—d^4F_4'	
09.300	H	2	27698.3	m^2D_2—a^4P_1	
02.038	H	6	27754.2	a^4D_4'—d^4D_4	
3599.135	H	6	27776.6	a^4D_4'—d^4F_5'	− .1
98.01	H	2*u*	27785.3	2^2P_2—5^2S	− .2
94.025	H	2	27816.1	m^2D_3—a^4P_3	
66.14	H	1*u*	28033.6	2^2P_1—5^2S	
46.45	H	1*u*	28189.2	a^4D_1'—c^2S_1	− .1
44.966	H	2	28201.0	a^2F_3—d^4P_2'	
33.744	H	4*u*	28290.5	a^2F_3—d^4G_4	
30.388	H	6	28317.4	m^2D_2—a^4F_3	
27.487	H	4	28340.7	a^2F_3—d^4D_3	.1
24.240	H	4	28366.8	a^2F_3—d^4F_4'	.1
20.032	H	4	28400.7	a^4D_1'—d^4F_2'	
17.029	H	2	28425.0	a^2F_3—d^4G_3	
12.122	H	4*u*	28464.7	2^2P_2—6^2D_2 a^4D_4'—d^4G_5	.1
07.38	Ex.	1	28503.2	a^4D_4'—d^4G_4	− .5
01.52	Ex.	1	28550.9	a^4F_2—d^4S_2	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs)
3501.31	Ex.	1	28552.6	a^4D_4'—d^4D_3	.4
00.314	H	2	28560.7	a^4D_2'—c^2S_1	
3498.063	H	2	28579.1	a^4D_4'—d^4F_4'	
88.864	H	2	28654.5	a^4D_2'—h_2	.1
87.565	H	2*u*	28665.1	a^2D_3'—c^2P_2'	
83.760	H	4	28696.4	a^4D_3—g_4	
81.9	Ex.	1*u*	28711.8	2^2P_1—6^2D_2	
75.998	H	4	28760.5	a^4D_2'—d^4F_3'	− .1
74.574	H	1	28772.3	a^4D_3'—d^4F_2'	
72.136	H	3	28792.5	a^4D_3'—h_2	
3463.5	H	1*u*	28864.3	2^2P_2—6^2S	− .2
59.424	H	1	28898.3	a^4D_3'—d^4F_3'	
57.856	H	3	28911.4	m^2D_3—a^4P_2	.1
50.335	H	6	28974.4	a^2D_3'—n_4	
40.52	H	3	29057.1	m^2D_2—a^4F_2	− .1
36.53	H	1*u*	29090.8	a^2D_2'—c^2P_2'	− .2
33.98	Ex.	1	29112.4	2^2P_1—6^2S	.1
20.16	H	1*u*	29230.1	a^2P_2—1_1	
14.2	Mu.		29281.1	2^2P_2—7^2D_3	−1.7
13.34	H	2	29288.5	a^2P_1—1_1	
02.222	H	3	29384.2	a^2P_2—c^2P_2'	
3396.324	H	1	29435.2	a^4F_3—c_3	
−95.473	H	2	29442.5	a^2P_1—c^2P_2'	
92.95	K	2	29463.2	a^2P_1—e^4D_2?	− .3
92.01	H	1*u*	29472.6	a^2F_3—h_2	
85.4	Sh.		29530.2	2^2P_1—7^2D_2	−2.4
84.815	H	2*u*	29535.3	a^4F_3—d_3	.1
81.425	H	3	29564.9	a^4F_3—c^2G_4	
79.69	Ex.	1	29580.1	a^4F_2—d^4P_1'	.4
75.671	H	2	29615.3	a^4F_3—d^4P_2'	
65.353	H	4*r*	29706.1	a^4F_4—c^2G_5	
58.76	Ex.	1	29764.4	a^4F_2—d^4D_3	.1
58.31	Ex.	1	29768.4	a^4D_2—e^4D_3	.1
54.475	H	2*u*	29802.4	a^4D_4'—d^4F_2'?	.1
53.8	Mu.		29808.4	2^2P_2—8^2D_3	−2.0
49.287	H	4*u*	29848.6	a^4F_2—d^4G_3	.1
42.85	K	1*u*	29906.0	a^4D_3'—e^4D_3	.4
37.850	H	6	29950.8	m^2D_3—a^4F_4 a^4F_5—c^2G_5	.1 − .4
35.235	H	3	29974.3	a^4F_4—c^2G_4	
29.638	H	4	30024.7	a^4F_4—d^4P_3'	
3326.2	Mu.		30055.7	2^2P_1—8^2D_2	− .9
19.691	H	4	30114.7	a^4F_4—d^4D_4	
17.225	H	4	30137.0	a^4F_4—d^4F_5'	
13.2	Mu.		30174.1	2^2P_2—9^2D_2?	−6.6
11.00	H	1*u*	30193.7	a^4D_1'—1_1	− .1
07.952	H	8	30221.5	a^4F_5—d^4G_6	
3292.903	H	3*R*	30359.6	a^4F_5—d^4D_4	− .6
.81	K	2	30360.5	m^2D_2—a^4F_3	− .2
.392	H	2	30364.3	a^4F_3—d^4P_2'	
90.549	H	4	30381.3	a^4F_5—d^4F_5'	
82.716	H	4	30453.8	a^4F_3—d^4G_4	
79.823	H	3	30480.7	m^2D_2—a^2F_3 a^4D_4'—e^4D_4	 .4
77.311	H	2	30504.1	a^4F_3—d^4D_3	
73.967	H	10*R*	30535.2	1^2S—2^2P_1	
68.278	H	3	30588.4	a^4F_3—d^4G_3	− .1
66.014	H	3	30609.6	a^2F_4—n_4	

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs)
3252.22	H	2	30739.4	$a^4P_2-d^4S_2$ $a^4D_2'-e^4D_2$?	− .1 .2
47.550	H	10*R*	30783.6	$1^2S-2^2P_2$	
43.160	H	4*u*	30825.3	$a^4F_4-d^4G_5$	
39.16	H	1*u*	30863.3	$a^4F_4-d^4G_4$	− .1
35.712	H	4	30896.2	$a^4F_3-h_2$	.1
33.89	H	2	30913.6	$a^4F_4-d^4D_3$	− .1
31.17	H	4	30939.6	$a^4F_4-d^4F_4'$ $a^4P_1-d^4P_1'$	− .4
26.60	H	2*u*	30983.5	$a^4P_1-d^4P_2'$	− .1
24.653	H	3	31002.2	$a^4F_3-d^4F_3'$	− .1
23.424	H	3*u*	31014.0	$a^4F_3-d^4F_2'$	
.044	H	1*u*	31017.7	$a^4F_5-d^4P_2'$?	.3
18.23	H	1*u*	31064.0	$a^4P_2-d^4P_3'$	.1
17.64	H	1*u*	31069.7	$a^4F_5-d^4G_5$	− .1
3209.47	H	1*u*	31148.8	$a^4D'_1-e^4D_1$	− .1
08.236	H	4	31160.8	$m^2D_3-a^4D'_3$	
3194.103	H	6	31298.7	$m^2D_2-a^4D_2'$	
71.658	H	1*u*	31520.2	$a^4D_2'-e^4D_1$	.1
69.690	H	4*u*	31539.7	$a^4F_3-g_4$	
60.047	H	2	31636.0	$a^4F_4-h_2$	− .1
56.623	H	3	31670.3	$m^2D_2-a^4D_1'$	
49.501	H	2	31741.9	$a^4F_3-d^4F_3'$	− .2
46.821	H	4*u*	31768.9	$a^4P_2-d^4P_1'$	
42.434	H	6	31813.3	$a^4P_2-d^4P_2'$	− .2
40.318	H	4	31834.7	$a^4P_2-d^4S_2$	
28.692	H	4	31953.0	$a^4P_2-d^4D_3$	− .1
26.106	H	6	31979.4	$a^4P_2-c_3$	
20.452	H	2*u*	32037.4	$a^4P_2-d^4G_3$	− .3
18.355	H	1	32058.9	$a^4D_4'-n_4$	
16.345	H	4*u*	32079.6	$a^4P_2-d_3$	
13.468	H	2	32109.2	$a^4P_2-c^2G_4$	− .1
08.603	H	6*r*	32159.5	$a^4P_2-d^4P_2'$	
3099.922	H	4	32249.6	$a^4P_2-d^4D_4$	− .1
93.993	H	6	32311.3	$m^2D_3-a^4D_4'$	.1
88.121	H	3	32372.8	$a^4P_1-d^4F_2'$	− .1
73.803	H	4	32523.6	$m^2D_3-a^2F_3$	
68.912	H	2	32575.4	$m^2D_2-a^2P_1$	
63.416	H	6	32633.8	$m^2D_2-a^2P_2$	
52.52	Ex.	1	32750.3	$a^4F_3-e^4D_3$	− .5
44.032	H	2	32841.6	$a^4F_4-e^4D_4$	
36.105	H	6	32927.4	$m^2D_2-a^2D_2'$	
30.25	H	2*u*	32991.0	$a^4P_2-c^2S_1$	− .2
24.993	H	2	33048.3	$a^4P_2-d^4D_3$	
22.608	H	3	33074.4	$a^4P_2-d^4F_4'$	
21.56	H	3*r*	33085.9	$a^4F_5-e^4D_4$	
14.84	H	2*u*	33159.6	$a^4F_4-e^4D_3$	− .4
3012.02	H	3*u*	33190.7	$a^4P_2-d^4F_3'$	− .2
10.840	H	5	33203.7	$m^2D_3-a^4D_3'$	
2998.384	H	2	33341.6	$m^2D_3-a^4D_2'$	
97.363	H	4	33353.0	$m^2D_2-a^2D_2'$	− .1
82.77	H	1*u*	33516.1	$a^4D_4'-o_4$	
79.38	H	2*u*	33554.3	$a^4D_4'-p_4$	
78.293	H	2*u*	33566.5	$a^4D_4'-q_4$	
61.177	H	6	33760.5	$m^2D_3-a^2F_4$ $a^4F_2-e^4D_1$	.2 −1.4
51.3	H	1*u*	33873.5	$2^2P_2-c^2D_3$	.4

TABLE X (*Continued*)

λ	Authority	Intensity	ν	Designation	ν(calc) − ν(obs)
2923.27	Ex.	1	34198.3	a^4P_2—e^4D_3	.3
11.21	H	1*u*	34340.0	a^4P_1—e^4D_2?	− .2
2882.937	H	4	34676.7	m^2D_3—a^2P_2	
58.737	H	2	34970.2	m^2D_2—a^2D_2'	.1
.233	H	1	34976.4	a^4P_2—e^4D_4	
− 46.49	Ex.	1	35120.7	a^4P_1—e^4D_1	
24.375	H	8	35395.7	m^2D_2—a^2D_2'	.1
2786.52	Ex.	1	35876.5	a^4F_4—o_4	.1
83.55	H	2*u*	35914.8	a^4F_4—p_4	− .1
82.61	H	2*u*	35926.9	a^4F_4—q_4	.1
66.388	H	8	36137.6	m^2D_3—3^2P_2	
2630.002	H	2	38011.5	a^4P_2—o_4	− .1
27.37	H	1	38049.5	a^4P_2—p_4	
26.6	Ex.	1*u*	38060.7	a^4P_2—q_4	1.1
18.381	H	10*r*	38180.2	m^2D_2—3^2P_2	.3
2494.88	K	2	40070.0	2^2P_2—d^4S_2?	− .3
92.142	H	8	40114.0	1^2S—a^4P_2	
41.625	H	6	40943.9	1^2S—a^4P_1	− .2
− 06.661	H	6	41538.7	m^2D_2—e_2'	
− 2392.629	H	8*r*	41782.3	m^2D_2—d_2'	
69.891	Mi.	6	42183.1	m^2D_2—4^2F	− .5
− 63.21	H.M.	1*u*	42302.6	1^2S—a^4F_3	− .2
19.575	H.M.	4	43098.1	m^2D_2—c_2'	− .2
2303.134	Mi.	6	43405.7	m^2D_2—b^2F_3	.2
− 2293.847	H.M.	8*R*	43581.4	m^2D_3—e_3'	.2
81.09	P.M.	2	43825.1	m^2D_3—d_2'	.1
63.11	H.M.	6*R*	44173.3	m^2D_2—a_1'	− .1
− 60.51	H.M.	4	44224.1	m^2D_2—4^2F	1.4
− 44.26	H.M.	2	44544.3	1^2S—a^4D_2'	− .2
− 38.45	H.M.	2*u*	44659.9	m^2D_2—5^2F	2.7
36.24	H.M.	1*u*	44704.0	m^2D_2—b^2P_2	− .2
− 30.10	H.M.	6*R*	44827.1	m^2D_3—b^2F_4	.1
− 27.77	H.M.	6*R*	44874.0	m^2D_2—b^2D_3'	− .1
25.691	H.M.	2*R*	44915.9	1^2S—a^4D_1'	− .2
15.68	H.M.	4*R*	45118.8	m^2D_2—b^2P_1	
14.59	H.M.	6*R*	45141.0	m^2D_3—c_2'	− .2
2199.76	Sh.	3*R*	45445.3	m^2D_2—b^2D_2'	.1
− .60	Sh.	3*R*	45448.6	m^2D_3—b^2F_3	.2
− 81.71	H.M.	1*u*	45821.2	1^2S—a^2P_1	− .4
78.95	H.M.	1*u*	45879.3	1^2S—a^2P_2	− .1
69.53	H.M.	2*u*	46078.4	m^2D_2—b_4'	− .2
65.10	H.M.	1*u*	46172.7	1^2S—a^2D_2'	.1
40.66	P.M.	2	46699.8	m^2D_2—5^2F ??	5.7
− 38.50	H.M.	1*u*	46747.0	m^2D_3—b^2P_2	− .3
30.76	H.M.	1	46916.7	m^2D_2—b^2D_2'	.1
19.87	P.M.	0	47157.7	m^2D_2—b^2P_1 ??	3.5
− 05.12	Sh.		47488.1	m^2D_2—b^2D_2'	.2
2024.33	Sh.		49383.0	1^2S—3^2P_2	

Authorities

A	Aretz.	K	Kayser.
C.T.	Crew & Tatnall.	M	Meggers.
Ed.	Eder & Valenta.	Mu.	Mulliken.
Ex.	Exner & Haschek.	R	Randall.
H	Hasbach.	Sh.	Shenstone.

H.M. Hasbach, with Mitra corrections.
P.M. Pina, with Mitra corrections.

able error between calculated and observed wave-numbers has been considered greater where such less reliable measurements have been used. In the ultraviolet below λ2369, the standard measurements of Mitra[9] have been accepted as correct with the exception of λ2148. Hasbach's wave-lengths have then been corrected by interpolation. This amounts to considering that his wave lengths are consistent but have a gradually increasing error. The justification for such a procedure is given by the small error between the calculated and observed wave-numbers. The tables used were Kayser and Konen "Handbuch der Spectroscopie" Vol. VII and Kayser Vol. V. The frequencies have all been re-calculated using Kayser's "Tabelle der Schwingungszahlen."

The number of lines classified is about 350. They include practically every strong line in the spectrum, as well as a great majority of the weak lines. The only comparatively strong unclassified lines from Meggers and Hasbach's lists, are the following:—

3454.70	(4*u*)
3382.899	(3)
3175.73	(3*u*)
2768.89	(3)

In the ultra-violet one low-voltage line alone, λ2171.75, remains unaccounted for, it is undoubtedly due to a term combining either with m^2D_2 or m^2D_3 and with none of the other known terms of the spectrum.

This research has been carried out in the Palmer Physical Laboratory of Princeton University. The writer wishes to express his gratitude for the co-operation of the other members of the department, and for the facilities and time which made the work possible. He is particularly indebted to Professor H. N. Russell, of the Department of Astronomy, who took the greatest interest in the progress of the work and to whom are due many of the ideas contained in this paper.

PRINCETON UNIVERSITY,
June, 1926.

THE TIME INTERVAL BETWEEN THE APPEARANCE OF SPECTRUM LINES IN SPARK AND IN CONDENSED DISCHARGES*

By J. W. Beams

Abstract

The experimental method consisted essentially in a comparison of the time interval elapsing between the appearance of two spectrum lines with the time required for light to travel a measured distance. The time intervals between the appearance of the bright visible spectrum lines of cadmium, magnesium and zinc in the spark in air and nitrogen and hydrogen in condensed discharges at various pressures were measured. The results indicate that the time between the appearance of these lines is due to atomic phenomena, and emphasize the importance of the final energy levels as well as the initial energy levels in determining the average time between excitation and the beginning of emission.

IT has long been known that the spectrum lines in a spark between metallic electrodes in air do not all appear simultaneously. In previous work,[1] however, owing to the very short time interval between the appearance of most of the lines and to the low resolving power of the instruments used, many of the lines appeared simultaneously. Also since the rate of increase of intensity of different lines varies considerably the results might be somewhat in error due to the lack of sensitivity of the photographic plate. Recently[2] the sequence of the appearance of the visible spectrum lines of cadmium and magnesium have been investigated by a modification of a method first used by Abraham and Lemoine[3] for measuring short time intervals. This work has been continued and extended to the determination of the actual time intervals between the appearance of the various spectrum lines, and this paper gives the results for the visible region of cadmium, magnesium, zinc, nitrogen and hydrogen.

The experimental method has been considerably refined since it was first described,[2] making it necessary to outline it briefly here. K (Fig. 1a) is a so-called Kerr cell, made by immersing two parallel plates of copper in carbon disulphide. N_1 and N_2 are crossed Nicol prisms, the diagonals of N_1 making an angle of 45° with the plates of K. If an electric field is applied across the plates of K, light passes N_2; but no light passes N_2 if

* National Research Fellow.

[1] See Baly, "Spectroscopy," p. 406 (1912).

[2] Brown and Beams, J.O.S.A. **11**, 11 (1925).

[3] Abraham and Lemoine, Comptes Rendus **129**, 206 (1899).

the field is relaxed.[4] If now the electric field in K is relaxed by a spark placed in front of N_1 and if the leads from K to the spark gap are very short, the field in K is relaxed before any visible light from the spark reaches it and no light passes N_2. If now the leads from the gap to K are lengthened, light passes N_2; if it is viewed in a spectroscope, the various spectrum lines are found to appear in a definite sequence. The arrangement N_1KN_2 then acts as a light shutter, the closing of which can be advanced or retarded with respect to a spark by simply lengthening or shortening the leads from the spark gap to K. The quick closing of this

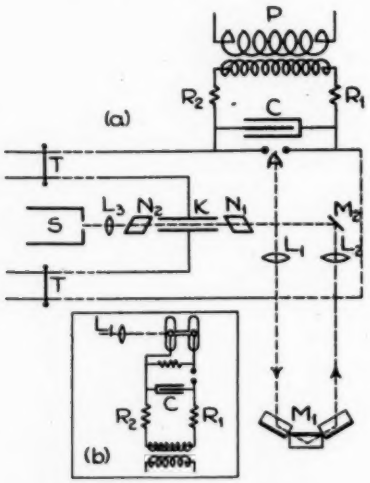


Fig. 1. Diagram of apparatus.

shutter results from the fact that the electric double refraction in K varies as the square of the voltage across the plates of K, and from the fact that the damping stops effective oscillations in K after the initial discharge. P is a sixty cycle ten thousand volt transformer, R_1 and R_2 non-inductive resistances, C a variable capacity which serves to brighten the spark at A. TT are cross wires which slide on the long leads from A to K. M_1 is a trihedral mirror system designed by Professor Hoxton, which is movable along a track parallel to the light path indicated and reflects the light from A accurately to the center of L_2 regardless of slight irregularities in the track upon which it slides. Both TT and M_1 are adjusted by the observer at S without the necessity of removing his eye from the position of observation. Several different spectroscopes, each with large light-gathering power, were used at S for the visual and photographic observa-

[4] Kerr, Phil. Mag. 1, 337 (1875).

tions. The photographs were taken on Wratten and Wainwright panchromatic plates hypersensitized with ammonia.

The metal whose spectrum is to be studied is placed in the terminals of the spark gap A. Light from A, made parallel by the lens L_1, is reflected from the movable mirror system M_1 through the lens L_3 and comes to focus at the center of K. The lens L_3 collects the light on the slit of the spectroscope, where the light is either viewed visually or photographed. M_1 is first moved a considerable distance from A and the shutter retarded until light just passes N_2. This light is composed of only a single line of the spectrum. If now the mirror system is moved forward, thus shortening the optical path from spark to shutter, the other spectrum lines one by one come into view. If then the distance that M_1 is moved forward between the appearance of any two spectrum lines is noted, the time interval between their appearance can be found by dividing the difference in light path by the velocity of light.

In studying the spectrum of hydrogen, the spark was between brass electrodes in a large glass tube filled with hydrogen at atmospheric pressure, with steam or with water gas. These lines were broad but quite intense. At lower pressures in the case of both hydrogen and nitrogen a short discharge tube was placed in the position of the spark gap so that its capillary was viewed end on. The tube was connected as shown in Fig. 1b, with a non-inductive resistance across its terminals to eliminate flashing while the potential was being built up. The capillary was very short and the tube as nearly symmetrical as possible. This is necessary in an alternating current discharge because of the finite velocity of the propagation of luminosity from anode to cathode, which varies with the constants of the circuit.[5] (This phenomenon was hurriedly investigated, and the results were in agreement with those of other investigators.[6])

The values given in the table are probably the result of atomic phenomena, and independent of the conditions of excitation within the limits of experimental error.[7] These conditions were varied considerably by changing the capacity in parallel with K, by replacing the carbon disulphide in the Kerr cell by chloroform and by changing the pressure in the discharge tube in the case of hydrogen and nitrogen, but no change in the measured time intervals could be detected. The precision of the above results is at least 0.3×10^{-8} sec., but varies somewhat for different lines because the sensitivity of the eye and photographic plate is not

[5] J. J. Thomson, "Recent Researches in Electricity and Magnetism," p. 115 (1893).
[6] Whiddington, Nature **116**, 506 (1925)
[7] Beams, Phys. Rev. **27**, 805(A), 1926.

TABLE I

Time intervals between appearance of spectrum lines.

	Wave-length		Classification	Intensity	Interval (sec.×10⁸)
			Magnesium spark		
1	4481	spark	$3d_{1,2}$—$4f$	10	
2	5184,73,67	arc	$2p_{1,2,3,}$—$2s^8$	10	8.2
			Cadmium spark		
1	5337,78	spark	$(5d_1$—$4f_1)$ $(5d_2$—$4f_2)$[9]	10	
2	4800	arc	$2p_2$—$2s^7$	9	12.
3	5086	arc	$2p_1$—$2s^7$	9	1.3
4	4678	arc	$2p_3$—$2s^7$	8	0.7
			Zinc spark		
1	4912,24	spark	$(4d_1$—$4f_1)$ $(4d_2$—$4f_2)$[10]	10	
2	4680	arc	$2p_3$—$2s^8$	8	15.
3	4722	arc	$2p_2$—$2s^8$	9	2.
4	4811	arc	$2p_1$—$2s^8$	9	1.3
			Magnesium-cadmium and cadmium-zinc spark		
1	4481 Mg	spark	$3d_{1,2}$—$4f$		
2	5337,78 Cd	spark	$(5d_1$—$4f_1)$ $(5d_2$—$4f_2)$		7.5
3	4912,24 Zn	spark	$(4d_1$—$4f_1)$ $(4d_2$—$4f_2)$		9.6
			Hydrogen discharge tube and spark in hydrogen		
1	4861		*H* beta	10	
2	4340		*H* gamma	8	6.
3	6563		*H* alpha	10	13.3 (?)
			Nitrogen discharge tube and spark in hydrogen		
1	5011	p_2—s^{10}	*N* II	2	
	5008[11]			4	
	5005[11]			8	
	5003	p_3—s^{10}	*N* II	10	
					0.8
2	5045	p_1—s^{10}	*N* II	6	
					0.2
3	4643	p_1—$p_2'^{10}$	*N* II	10	
	4641	enhanced[11]		8	
	4631	p_1—$p_1'^{10}$	*N* II	10	
					0.6
4	4803	d_1—$d_1'^{10}$	*N* II	9	
	4788	d_2—$d_2'^{10}$	*N* II	8	
	4781	d_2—$d_1'^{10}$	*N* II	7	
	4448	ordinary[12]		10	
	4433	ordinary[12]		8	
					0.3
5	4531	ordinary[12]		7	
	4515	enhanced[12]		6	
					0.8
6	5679	p_1—d_1^{10}	*N* II	10	
	5676	p_3—d_3^{10}	*N* II	6	
	5667	p_2—d_2^{10}	*N* II	8	
					0.2
7	5942	p_1'—d_1'	*N* II	8	
	5932	p_2'—d_2'	*N* II	8	

[8] Revised Paschen notation.

[9] Salis, Ann. d. Physik **76,** 145 (1925).

[10] Fowler, Proc. Roy. Soc. **A107,** 31 (1925).

[11] Kayser, "Handbuch der Spectroscopie."

[12] Fowler, Monthly Notices **70,** 692 (1920).

uniform over the spectral region investigated. However, with the exception of the red region the sensitivity of the eye is greatest where that of the photographic plate is least, which gives a check upon intensity errors. The observations on hydrogen are less precise, because of the red color of H alpha.

It is easily seen from the table that the appearance of the lines is not in the order of increasing wave-lengths or in the order of integrated intensities, yet the value of the intensity of any given line usually varies over such wide ranges during the discharge that the integrated intensity is not a measure of its actual intensity at the time of observation. In the case of magnesium, cadmium and zinc, at least, the spark lines appear before the arc lines. In the sharp arc triplet of zinc the members appear in the order of increasing wave-lengths, while in the corresponding triplet in cadmium the sequence is different.

In the processes connected with the emission of each of the members of the above triplets the electron falls from the same $2s$ energy level to different $2p_{1,2,3}$ energy levels so that the sequence in the time of appearance of the lines of these triplets indicates definitely the importance of the final energy level ($2p_{1,2,3}$ in this case) in determining the average time between excitation and the beginning of emission.* The same kind of a result is also found in NII spectrum where the d—d' group appears before the p'—d' group. It will be noted that in the NII spectrum, the p—s group appears before the p—p' group and the latter before the p—d group. In the emission of these groups the electron falls from different initial energy levels to the same final energy levels so that this sequence illustrates the well known importance of the initial energy level in determining the time of the beginning of emission. Unfortunately the resolving power of the spectroscopes used was not sufficient to determine the time of appearance of the different members of the above groups of NII.

A photometric study of the rate of increase of intensity of the members of the zinc and cadmium triplets and an extension of the present work into the ultra-violet region are now in progress and promise to give more

* In emphasizing the importance of the final energy level in determining the time of the beginning of emission, the above results suggest, although they do not prove, that the electron might not remain in the initial energy level the total time between excitation and emission, but falls to the final energy level and remains a definite average time there before the energy is radiated.

information on the processes taking place between excitation and emission.

In conclusion I should like to express my thanks to Professors C. M. Sparrow, L. G. Hoxton and F. L. Brown for many valuable suggestions and criticisms, and to Mr. A. J. Weed, instrument maker, for help in the construction of apparatus.

ROUSS PHYSICAL LABORATORY,
UNIVERSITY OF VIRGINIA,
June 7, 1926.

ELECTRONIC STATES AND BAND SPECTRUM STRUCTURE IN DIATOMIC MOLECULES. I. STATEMENT OF THE POSTULATES. INTERPRETATION OF CuH, CH, AND CO BAND-TYPES

By Robert S. Mulliken

Abstract

The problem of the interpretation of band-structure from combination relations; ambiguities and criteria for overcoming them. In the analysis of band spectra, it may often be assumed that each observed frequency is due to a combination of terms whose rotational energy parts are of the form $F(j)=Bm^2+\cdots=B(\sqrt{j^2-\sigma^2}-\rho)^2+\cdots$ (Kratzer-Kramers and Pauli term); here j is the quantum number corresponding to the total angular momentum, $mh/2\pi$ is the nuclear angular momentum, $eh/2\pi$ and $\sigma h/2\pi$ are electronic angular momentum components parallel and perpendicular to m, σ being also parallel to the internuclear axis. In the empirical analysis of band-structure in accordance with the combination principle, only *differences* such as $\Delta_1F(j)=F(j+1)-F(j)$ and $\Delta_2F(j)=F(j+1)-F(j-1)$ can be obtained. If derived from terms of the Kratzer-Kramers and Pauli type, these are (after expanding to remove the radical) of the forms $\Delta_1F(j)=2B(T+\frac{1}{2})-B\rho\sigma^2/j(j+1)+\cdots$ and $\Delta_2F(j)=4BT-2B\rho\sigma^2/(j^2-1)+\cdots$, where $T=j-\rho$ is defined as the **apparent or effective rotational quantum number.** Similarly, the most general expression (after expansion to remove the radical) for any band-branch is of the form $\nu=A+B'(\Delta T)^2+2B'T''\Delta T+(B'-B'')T''^2+f(j)+\cdots$; primes here refer to the more excited, double primes to the less excited state; $\Delta T=T'-T''$; $f(j)=(\rho'\sigma'^2/j'^2-\rho''\sigma''^2/j''^2)$. **P-form, Q-form, and R-form branches are defined** as branches for which $f(j)$ is zero and ΔT has the respective values -1,0 and $+1$; these are of the forms assumed by P, Q, and R branches ($\Delta j=-1,0,+1$) for the (usual) special case $\Delta T=\Delta j$. In case ρ and σ are simultaneously present and large enough so that the small $\rho\sigma^2$ term is experimentally detectable, the values of j, ρ, and σ can be determined directly if sufficiently accurate measurements are feasible. But in the usual case that one (or both) of the quantities ρ and σ are zero or nearly so, it is evidently impossible to determine j, ρ, and σ without the aid of additional information or assumptions, since the ΔF's and the forms of the branches are now functions of T' and T'' alone; in such cases it has ordinarily been tacitly assumed in the past, very often erroneously according to the present work, that $\sigma=0$. Criteria are discussed for overcoming these ambiguities of interpretation. These are (a) the presence or absence of Q branches (b) especially valuable, the absence of particular lines ("*missing lines*") near the band-origin, and finally (*c*) the postulates stated below.

Interpretation of bands of the CuH, HCl, CH, and CO types, and statement of the postulates. Recent work on the classification of electron levels in molecules in analogy with those of atoms is discussed; the NOγ bands (third positive nitrogen bands) are classified as $^2S\rightarrow{}^2P_{1,2}$ transitions and it is suggested that

Jevons' SnCl bands are due to the transition $^2S \rightarrow {}^2P_{1,2}$ in the Sn^+ ion in Sn^+Cl^-. The quantities ϵ and σ of the Kratzer-Kramers and Pauli formula are interpreted as components of an *electronic inner quantum number* j_e for the molecule as a whole, or in some cases as individual inner quantum numbers j_e for the two atoms of the molecule; in all cases it is found possible to assume that the j_e values for molecular states are identical with *Sommerfeld's* j values for corresponding atomic states.—Kratzer's interpretation of the violet CN bands (j = integral, $j_e = \rho \sim \pm\frac{1}{2}$ for both initial and final states) is adopted with slight modification; in addition, these bands are ascribed to a $^2S \rightarrow {}^2S$ transition, probably of a single outer electron. The same interpretation applies to a number of analogous band spectra, emitted by BO, CO^+, N_2^+, SiN, and AlO. The CuH, AgH, and AuH bands, and the infrared halogen halide bands, hitherto classed as essentially similar to the violet CN bands (all these bands have P- and R-form P and R branches only), are now interpreted as due to $^1S \rightarrow {}^1S$ electronic transitions, with j = half-integral, and $j_e = 0$ for both initial and final states; the infrared CO bands probably have the same structure. This new interpretation makes understandable the single character of the lines in bands of the CuH type, as compared with the doublets of CN, and at the same time gives expression, in the j and j_e values, to the contrasting facts that CN contains an odd number of electrons, and molecules like CuH and HCl an even number. The importance of Kratzer's analysis of the CH bands (j = integral, $\rho' = \pm\frac{1}{2}$, $\sigma' = 0$, — the value of σ' represents a revision of Kratzer's $\sigma' = \frac{1}{2}$, — $\rho'' = \pm\frac{1}{2}$, $\sigma'' = 1$) is emphasized. Since CH is an odd molecule like CN, the analysis confirms the possibility of $\rho = \pm\frac{1}{2}$ and of j = integral for odd molecules, which were *assumed* by Kratzer in the case of CN. The presence of Q branches may be attributed to the presence of σ''. The values $\rho'' = \pm\frac{1}{2}$ and $\sigma'' = 1$ are respectively attributed to the H atom in its normal state and to the C atom in a ^1P excited state; the normal state of H is thereby classified as ^2S, as for the alkali metals, in confirmation of recent work in line spectra.—The observed structure of the CO Angstrom bands, including the presence of Q branches and the characteristic missing lines, is explained by the assumptions j = half integral (in accord with the assumptions made for CuH and other even molecules), $\rho' = 0$, $\sigma' = 0$, $\rho'' = 0$, $\sigma'' = 1$. The values of j_e here ($j_e' = 0$, $j_e'' = 1$) are in complete agreement with Birge's interpretation of these bands, based on entirely different grounds, as $^1S \rightarrow {}^1P$.—With but slight generalization, the leading assumptions and conclusions involved in the above interpretations can be stated in the form of three simple postulates, which are stated on p. 503 (*q.v.*) and will not be repeated here. With the help of these postulates, a systematic interpretation of most known band spectra is possible. As a corollary of the postulates it is concluded that the normal state of all *diamagnetic gases* (H_2, N_2, CO, HCl, etc.) is probably a ^1S state ($j_e = 0$); the paramagnetism of NO is attributed to its double ^2P normal state ($j_e = \sigma = \frac{1}{2}$ and $1\frac{1}{2}$), while that of O_2 is perhaps due to a ^3S normal state ($j_e = 1$). An incidental result of the postulates is the disappearance of quarter-integral values of j and j_e.

Introduction

IN the development of the quantum theory of band spectra, the diatomic molecule was first treated as a simple rotator, then as a rotating harmonic oscillator, later as an anharmonic oscillator. Finally certain quantities ϵ and σ were introduced which are of the nature of electronic quantum numbers; and independently, evidence was found

from other considerations for classifying various molecular electronic states in analogy to certain atomic states. It is with the correlation of these two last-mentioned phases of development, and the deduction of consequences from the results obtained, that the present series of papers is chiefly concerned.

The subject has already been discussed briefly in a preliminary paper.[1] Three postulates were there proposed which seem capable of accounting better than heretofore for many features of molecular spectra, and which also give results having a bearing on atomic spectra. The postulates were applied in a second paper[2] to the spectra of ZnH, CdH, and HgH. In the present paper, the empirical situation leading up to the formulation of the postulates is first discussed in more detail and from a somewhat different point of view. The postulates and some of their consequences are then presented and discussed. Definite interpretations (mostly different from those hitherto usual) are also given, in this and succeeding papers, for a large number of band spectra concerning which much uncertainty has existed, and in this way a very marked unification and systematization of the empirical side of the subject is obtained.

The first sections of the paper (up to p. 497) are devoted largely to a review of a number of empirical and theoretical relations which form a necessary foundation for the later discussion. Various new or hitherto insufficiently emphasized conclusions and relations are brought out; and at the same time a notation is set up.[3]

For a more general discussion of the quantum theory of band spectra reference should be made to Sommerfeld's "Atombau," 4th Edition,[4] and to a recent account by Kratzer,[5] or especially to the very complete treatment in the forthcoming National Research Council report.[3] Reference may also be made to several briefer reviews of the subject in which the empirical situation in regard to known band spectra is

[1] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 144 (1926). The statements made on p. 144 of ref. 1 in regard to the occurrence of $\Delta j=0$, and on p. 145 in regard to three special cases of Q branches, are partially incorrect, and should be disregarded.

[2] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 151 (1926).

[3] The notation used is intended to conform as closely as possible to that adopted by the National Research Council Subcommittee on Radiation in Gases for their report on band spectra. It differs in one or two points (definitions of Δj and ΔT) from that used in refs. 1 and 2.

[4] A. Sommerfeld, "Atombau and Spektrallinien," 4th ed., chap. 9 (1924).

[5] A. Kratzer, Enzyklopedie der Math. Wissenschaften **5**, 821–59 (1925).

considered.[6,7,8] Reference should also be made to a brief review of a more theoretical nature by Kratzer.[9]

Matters related to the vibrational states of molecules and their changes will be largely subordinated in the present series of papers, since the correlations established are primarily between band-structure, which is qualitatively practically independent of the vibrational quantum number, and molecular electronic states.

Quantum Theory of Band Spectra: Rotational Energy and Fine Structure of Bands

Energy and spectroscopic terms of a molecule. For the rotating anharmonic oscillator, application of the quantum theory leads to the following familiar expression[4] for the energy contribution E^m due to rotation, m being the quantum number associated with the nuclear rotation, n the vibrational quantum number, and J the moment of inertia. Since in the analysis of spectra, wave-number units are ordinarily used, it will be convenient to use $F(m)=E^m/hc$ rather than E^m. Then:

$$F(m)=E^m/hc=[h/8\pi^2cJ_0-\alpha n]m^2-Dm^4+\cdots=Bm^2+\cdots \qquad (1)$$

The total energy can be somewhat arbitrarily divided into (a) *electronic* energy E^e due to displacement of an electron from its normal orbit, (b) *vibrational* energy E^n, (c) *rotational* energy E^m. The term corresponding to the total energy of the molecule is then:

$$F=F(e)+F(n)+Bm^2+\cdots \qquad (2)$$

Energy changes and band structure. In general, corresponding to a combination of two terms of the form of Eq. (2), there is an emitted frequency which can be written as follows:

$$\Delta F=\Delta F(e)+\Delta F(n)+\Delta F(m)=\nu^e+\nu^n+\nu^m=\nu^0+\nu^m=\nu. \qquad (3)$$

All the bands emitted by a particular molecule and having a common value of ν^e (but differing values of ν^n and ν^m) are defined as a *band system*. Each different *band* corresponds to a different value of ν^n. In Eq. (3), ν^e often has more than one value for a single band-system, because of double or multiple electronic terms $F(e)$; these are analogous to multiplets in line spectra. The case $\nu^e=0$ corresponds to an infra-red oscillation-rotation band.

[6] R. Mecke, Phys. Zeit. **26**, 219 (1925). Especially valuable is the discussion of term-types and band-types, and the review of the experimental material.

[7] G. H. Dieke, Physica **4**, 193–218 (1924).

[8] R. Fortrat, J. de Phys. et le Radium **5**, 33 (1924).

[9] A. Kratzer, Naturwissenschaften **27**, 577 (1923).

In simple bands having $\Delta m = \pm 1$ (*e.g.*, the infra-red HCl bands), the equations for the lines of the two branches (respectively denoted the R and P branches) are of the form[4]:

$$\nu = \nu^0 + B' \pm 2B'm + Cm^2 + \cdots \qquad (C = B' - B''). \tag{4}$$

Here and in the following, *primes* attached to any symbol refer to a *higher*, *double primes* to a lower, energy level.

Kratzer's theory of rotational doublets of the violet CN *type; electronic quantum numbers; notation and combination rules for rotational terms of the violet CN type.* Empirically, the violet CN bands consist of a P and an R branch capable of being described by Eq. (4), using half-integral values of m, except for the fact that each line is split into a narrow doublet. This Kratzer explained[10,11] by assuming the existence of two slightly different rotational states for each value of m' and of m''. To account for this and the observed linear increase of the doublet separation with m (the doublets are unresolved near $m = 0$), he proposed the following revision of Eq. (1):

$$F(j) = Bm^2 + \cdots = B(j \mp \epsilon)^2 \pm 2\delta(j \mp \epsilon) + \cdots \tag{5}$$

[10] A. Kratzer, Münch. Ber., p. 107 (1922), and later papers, in particular, Ann. der Physik **71**, 72 (1923).

[11] It is desirable here to attempt to justify Kratzer's *assumptions*, as embodied in Eqs. (6) and (7) and the relation $\epsilon' = \epsilon'' = \frac{1}{2}$. In the first place, Kratzer's rule $\Delta\rho = 0$ might conceivably be replaced[5] by $\Delta\rho = +1$ or -1 (e.g., $\rho' = +\frac{1}{2}, \rho'' = -\frac{1}{2}$, or $\rho' = -\frac{1}{2}$, $\rho'' = +\frac{1}{2}$). But it is easily shown that the two resulting P branches would be double-P-form and Q-form, respectively (cf. p. 492) and that the resulting R branches would be Q-form and double-R-form; and such branches are not observed.

A change of sign of ρ during emission would, however, seem more plausible for Q branches, since it occurs in the Q branches of bands of the HgH type.[2] As Dieke has shown (Zeits. f. Physik, **33**, 161, 1925; Physica, **5**, 178, 1925), Q branches of this type would in CN be exactly (due to $\epsilon'' = \frac{1}{2}$ exactly) superposed one on the observed P_1, the other on the observed R_2 branch. While the existence of such P-form and R-form Q branches here cannot be directly disproved, it makes no connection with a reasonable model, and also fails to account for the observed equality of intensity of the doublet components (P_1, P_2 and R_1, R_2). On the basis of Kratzer's interpretation, the latter can be explained very naturally as due to equality in the à priori probabilities of F_1 and F_2 states.

If other values of $\epsilon' = \epsilon''$ than approximately $\frac{1}{2}$ are used in Eqs. (6), other interpretations of the violet CN bands result. Birge has suggested (Phys. Rev. **25**, 240, 1925) what is in effect $\rho' = \pm 0.00115$, $\rho'' = 0$, $j =$ half integral; no explanation is given, however, of the double value of ρ'. The values $\epsilon' = \epsilon'' \sim 1$ or $1\frac{1}{2}$, etc., are also possible. The strongest argument against other values of ρ than $\frac{1}{2}$ is that the latter is the only value which fits into a unified picture with results on other band spectra. The assumption $\epsilon' - \epsilon'' = \pm 1$ would lead to results similar to those for $\rho' - \rho'' = \pm 1$, $\epsilon' = \epsilon'' = \frac{1}{2}$, and meets with similar objections.

Another possibility, instead of $\rho = \pm\epsilon$, would be that ρ possesses two slightly differing positive values both near $\frac{1}{2}$.

Here j (the notation here used differs from Kratzer's) is $2\pi/h$ times the *total* angular momentum of the molecule, and is assumed to differ by $\pm\epsilon$ from m, the quantity ϵ being of the nature of an electronic quantum number. The two signs of ϵ correspond to parallel and anti-parallel positions of ϵ with respect to m. By assigning integral values to j, setting $\epsilon=\frac{1}{2}$, and giving δ a very small positive value, two nearly coincident values of $F(m)$ are obtained for each value of m. These correspond to $(j+1)-\epsilon$ and $j+\epsilon$, and give an explanation of the observed double terms.

The presence of a linear term in j, as used by Kratzer, is open to theoretical objections.[12] $F(j)$ can equally well be represented without this term, if ϵ values differing slightly from $\frac{1}{2}$ are used. The values $\epsilon'=0.49885$ or 0.50115, $\epsilon''=0.500$, suffice to account for the observed doubling in the violet CN bands (for not too large values of m), according to calculations of Birge.[13] In the following this interpretation of the bands will be used.

To avoid confusion, the symbol ρ will be used to embrace both $+\epsilon$ and $-\epsilon$; thus $\epsilon=|\rho|$. It will frequently be necessary in the following to distinguish between terms where $\rho=+\epsilon$ and those where $\rho=-\epsilon$. In agreement with Kratzer, the former will be called F_1 terms, the latter F_2 terms, thus

$$\begin{aligned} F_1(j) &= Bm^2+\cdots=B(j-\epsilon)^2+\cdots; \\ F_2(j) &= Bm^2+\cdots=B(j+\epsilon)^2+\cdots \end{aligned} \tag{6}$$

According to Kratzer, the four observed branches in the violet CN bands are then interpreted (cf. Eq. (3)) as in Eq. (7). It is important to note that *P and R branches are here defined in terms of changes of j, not of m.*

$$\begin{aligned} R_1(j)&=\nu^0+F_1'(j+1)-F_1''(j); \quad R_2(j)=\nu^0+F_2'(j+1)-F_2''(j) \\ P_1(j)&=\nu^0+F_1'(j-1)-F_1''(j); \quad P_2(j)=\nu^0+F_2'(j-1)-F_2''(j) \end{aligned} \tag{7}$$

The doublets are formed by $R_1(j+1)$ and $R_2(j)$, and by $P_1(j+1)$ and $P_2(j)$. This is because, with $\epsilon'=$approximately $\frac{1}{2}$, $F_1'(j+1)$ and $F_2'(j)$, and likewise $F_1''(j+1)$ and $F_2''(j)$ if $\epsilon''=$nearly $\frac{1}{2}$, are nearly equal (cf. Eq. (6)). Thus, although the pair of values (j', j'') differs for the two components of a doublet, the pair (m', m'') is practically the same for the two components. If $\overline{R}(m)$ and $\overline{P}(m)$ denote *mean values* for the two components of each doublet, Eq. (4) is then applicable to $\overline{R}$ and $\overline{P}$.

[12] R. T. Birge, cf. E. C. Kemble, J.O.S. **12**, 4 (1926), footnote on p. 4.

[13] As shown by Birge (Phys. Rev. **25**, 240 (1925)) and Dieke (Physica **5**, 178, (1925)), there is an error in the δ values given by Kratzer. The ϵ' and ϵ'' values given above are the result of unpublished calculations of Professor Birge.

Empirically, the structure is the same (aside from the doublets) as if $\rho=0$, $j=m=$ half-integral. For a more complete discussion, reference should be made to Kratzer's paper.[10,11]

It will be noted that, according to Eq. (7), combinations occur only between F_1' and F_1'', or F_2' and F_2'', but not between F_1' and F_2'' or F_2' and F_1'' terms. This is a rule which apparently always holds for P and R branches.

Electronic quantum numbers and the Kratzer-Kramers and Pauli formula for the rotational term. In his well-known 1919 paper, Lenz discussed the possibility of an electronic angular momentum (to which would correspond a quantum number which has more recently been designated by σ) around the figure axis, and deduced some of its consequences.[14] Kratzer,[9] and Kramers and Pauli,[15] later generalized this to include both a ρ and a σ (both assumed fixed in the molecule), as follows:

$$F(j)=Bm^2+\cdots=B(\sqrt{j^2-\sigma^2}-\rho)^2+\cdots \tag{8}$$

According to Kramers and Pauli, ρ in Eq. (8) should appear only with the positive sign, for reasons of dynamical stability; but Kratzer has shown that in various cases (*e.g.*, the CH bands and bands of the HgH type) the observed facts can be explained only by admitting $\rho=-\epsilon$ as well as $\rho=+\epsilon$, as in Eq. (6).

Four important special cases of Eq. (8) can conveniently be distinguished, as follows:

$$F(j)=B[(j-\rho)^2-\sigma^2+\rho\sigma^2/j+\ldots.]+\ldots\ldots \tag{8A}$$

$$F(j)=B(j-\rho)^2+\ldots. \tag{8B}$$

$$F(j)=B(j^2-\sigma^2)+\ldots. \tag{8C}$$

$$F(j)=Bj^2+\ldots. \tag{8D}$$

In the general case it is convenient to write Eq. (8) in the developed and expanded form of Eq. (8*A*), which represents a sufficient approximation except for the smallest values of j. An example involving case (8*B*) has just been discussed; examples involving the other cases, and the problem of distinguishing the various cases, will be considered below.

An important fact in Eqs. (6) and (8) is that it is not m, but j, which is quantized and which takes on a succession of integral or half-integral values. In fact, when σ is present the successive values of m are not even rational, and do not differ by integers.

[14] W. Lenz, Verhandlungen der Deutschen Phys. Ges. **21**, 632 (1919).
[15] H. A. Kramers and W. Pauli, Jr., Zeits. f. Physik **13**, 351 (1923).

Definition of j_e. It is convenient to have a symbol for the quantum number (if such it is) corresponding to the resultant electronic angular momentum of a molecule. This will now be denoted by j_e. In general, $j_e=\sqrt{\rho^2+\sigma^2}$, but in practice, either ρ or σ is usually approximately zero, and in known cases (e.g. CH and OH) where both ρ and σ are present, it proves to be more appropriate to speak of the molecule as having two j_e's, one for each atom. The necessity, which exists in the case of molecules, of distinguishing between j and j_e, obviously disappears in the case of atoms, but to minimize possible confusion, j_e rather than j will generally be used below in referring to atomic inner quantum numbers.

Definition of P, Q, and R branches. According to the correspondence principle,[4,9] the possible changes of j should be limited to $\Delta j=+1$ (R or positive branch),0 (Q or zero branch), and -1 (P or negative branch); here $\Delta j=j'-j''$. Frequently P, Q, and R branches are simultaneously possible, but for certain types of electronic transitions, one, or perhaps sometimes even two, of the three possible kinds of branches should be lacking.[9]

The significance of Q branches.[1] For oscillation-rotation band ($\nu^e=0$ in Eq. (3)), the presence of a σ is a necessary and sufficient condition for the presence of a Q branch.[4,9] In the case of electronic bands, the presence of a σ (either a σ' or a σ'' or both) appears to be a *sufficient* condition for the presence of a Q branch, for practically any reasonable type of motion of the emitting electron[16]; but it is *not*[15] a *necessary* condition. Conversely, when Q branches are lacking in an electronic band, we can be fairly sure that $\sigma'=\sigma''=0$, hence that the nuclear motion is a pure rotation. The *presence* of Q branches in an electronic band is on the other hand a strong indication, although not in general more than this, of the presence of a σ' or σ'' or both. In practise a σ' or σ'' seems always to be present when Q branches occur, and vice versa.

The Significance of Missing Lines

Terms of the σ type. The "missing lines" near the origin of a band should be of great value for the interpretation of band structure. In the case of rotational terms of the σ type (Eq. (8C)), the missing lines should

[16] If the motion of the emitting electron should happen to be a linear vibration along a line always perpendicular to both j and j_e, P and R branches should occur alone, even if a σ were present. But this case is very improbable.

[17] Cf. ref. 4, especially p. 745–46; it should, however, be noted that the H_2O and MgH_2 bands to which Sommerfeld makes reference are really in all probability OH and MgH bands.

be determined by the fact[14,15,17] that j cannot be less than σ (cf. Eq. (8)). This rule determines, for each homologous set of molecular terms, a minimum value of j, which will be denoted $j_{min.}$ The value of $j_{min.}$ should be that of the next integer or half-integer (according as the values of j are integral or half-integral,—cf. postulate III, p. 503) equal to or greater than σ. Thus $j_{min.}$ is of great value in setting close limits to σ, a quantity which for terms of the pure σ type (Eq. (8C)) is not otherwise open to experimental test (unless by such means as the Zeeman effect). The method of determination of $j'_{min.}$ and $j''_{min.}$ in practise is illustrated by the discussion of the CO bands (p. 501) and of bands of the HgH type.[2]

Terms of the ρ type. If $F(j)$ is of the ρ type (Eq. (8B)), there is some uncertainty as to the expected value of j_{min} for a given set of rotational terms. *For F_1 terms* (cf. Eq. (6)) $j=m+\epsilon$, and it seems fairly clear that the value of j_{min} should be that of the next integer or half-integer, as the case may be, equal to or greater than ϵ. *For F_2 terms*, where $j=m-\epsilon$, one would naturally expect j_{min} to have the smallest possible positive value, namely 0 or $\frac{1}{2}$, as the case may be. For both cases the relations just suggested can be considered as consequences of a *guiding principle* (or postulate) that for a *homologous series* of terms there should be at no point a reversal from a parallel to an anti-parallel orientation of m and ϵ: for it is precisely such a reversal which distinguishes the F_1 from the F_2 term-series.

Kratzer's exclusion of the state $j=0$. In his analysis of the violet CN and of the ZnH, CdH, and HgH bands,[10] Kratzer has arbitrarily excluded the state $j=0$ for both F_1 and F_2 terms. According to the principle of the preceding paragraph, the state $j=0$ is not possible for F_1 terms with $\epsilon=\frac{1}{2}$, but for F_2 terms it should be possible. In the last analysis, the *experimental* evidence for Kratzer's exclusion of $j=0$ for F_2 terms now consists[18] only in the probable absence of the line $R_2(0)$ in the HgH bands λ4017 and 4219; in the corresponding ZnH and CdH bands the evidence is inconclusive.[2] The line $R_2(0)$ would involve a state $F_2''(0)$; but if this is really absent, the fact might be attributed[2] to the presence of a σ'' in addition to ϵ''. In the violet CN bands (cf. Eq. (7)), the absence of $R_2(0)$ and $P_2(1)$, which respectively involve $F_2''(0)$ and $F'_2(0)$, has been *assumed* by Kratzer, but there is no experimental evidence[19] for (nor, perhaps, against) this assumption, since these lines cannot be

[18] The absence of lines such as $P_2(1)$ and $Q_2(0)$ in HgH was cited by Kratzer as evidence that $F_2'(0)$ must also be excluded arbitrarily. But this exclusion is now explained[2] as due to the presence of a σ'.

[19] In regard to possible evidence from intensity data, cf. R. T. Birge, Phys. Rev. 25, 240 (1925) and G. H. Dieke, Zeits. f. Physik 33, 161 (1925).

resolved from their respective doublet-companions $R_1(1)$ and $P_1(2)$. Finally, there is apparently conclusive direct evidence, in the data on the CH and OH bands, that the state $j=0$ actually occurs for F_2 terms; this evidence will be given in a later paper.

The null-line. The probable absence in HgH of $R_1(0)$, and the practically certain absence in the violet CN bands of the null-line, which corresponds to $R_1(0)$ plus $P_1(1)$, are adequately explained by the principle stated in the second preceding paragraph, since the lines mentioned would involve $F_1(0)$ terms.

Terms of the general Kramers and Pauli type. The values of $j_{min.}$ can be readily predicted here by an extension of the principles used above in the cases of ϵ-type and σ-type terms.

Ambiguities in the Correlation of Empirical and Theoretical Band Structures

Combination differences. In the analysis of band spectra, the application of the combination principle does not give directly $F(j)$, but only *differences* of this function. In practise, these are of two kinds. In bands having only P and R branches, and frequently also in other cases, the only type of difference that can be obtained is of the form[20]

$$\Delta_2F(j)=F(j+1)-F(j-1) \tag{10}$$

Such differences are obtained in bands of the violet CN type (cf. Eq. (7)) as indicated by Eq. (11), where $i=1$ or 2:

$$\Delta_2F_i'(j)=R_i(j)-P_i(j)\,;\quad \Delta_2F_i''(j)=R_i(j-1)-P_i(j+1) \tag{11}$$

In practise, the difference is formed between a particular pair of lines (one P and one R) suspected of having a common initial or final state, then between the next pair of lines, and so on. Similar differences are then formed in other bands of the same system. If the entire set of differences so formed for one band agrees, within the errors of measurement, with a corresponding set for another band having the same value of the final vibrational quantum number n'', these differences may be regarded as probably real $\Delta F''$'s. In case of accurate agreement for bands having the same n', the differences are probably real $\Delta F'$'s. To be rigorously certain of the reality of a set *either* of $\Delta F'$'s or of $\Delta F''$'s, it will be seen on close examination that it is necessary to obtain such quantitative agreements in the case of *both* sets.

[20] Of course $\Delta_2F(j)$ could alternatively be defined as $F(j+2)-F(j)$, but the form chosen is more convenient in practice.

When Q branches are present, additional combination relations frequently also exist from which differences of the following form can be obtained[6]:

$$\Delta_1 F(j) = F(j+1) - F(j). \tag{12}$$

These are obtained by appropriate combinations of P and Q, or of Q and R lines (cf. Eqs. (17) and (18)). They can be tested in the same way as the $\Delta_2 F$'s, but also, as will be seen from Eqs. (17) and (18), in another way requiring data only on a single band. The existence of combination relations can also be tested in various other ways which are often useful.[5]

Effective rotational quantum numbers. Setting $j-\rho=T$ in Eq. (8*A*), to give Eq. (8*E*), the following ΔF equations are readily obtained; in these equations the quantity T evidently plays an important part which is well described by calling it the "*effective rotational quantum number.*"

$$F(j) = Bm^2 + \cdots = BT^2 - B\sigma^2 + B\rho\sigma^2/j + \cdots \tag{8E}$$

$$\Delta_1 F(j) = 2B(T+\tfrac{1}{2}) - B\rho\sigma^2/j(j+1) + \cdots \tag{13}$$

$$\Delta_2 F(j) = 4BT - 2B\rho\sigma^2/(j^2-1) + \cdots \tag{14}$$

From Eqs. (13) and (14) it will be seen that from an observed set of ΔF's, absolute values of B, T, and T_{min} can be determined if good experimental data are available. One must of course first know whether the ΔF's are $\Delta_1 F$'s or $\Delta_2 F$'s, since otherwise B may be incorrectly evaluated and the T values be in error by a half unit; but there is seldom any difficulty on this score in practice. Empirically, T is usually *approximately* either an integer or a half-integer, or sometimes apparently a quarter-integer. It is important to note that in case $\sigma=0$, $T=m$; if $\epsilon=0$, $T=j$.

The empirical form of the ΔF's gives no information, however, in regard to the values of ρ, σ, j, and j_{min}, *unless* ρ *and* σ *are simultaneously present* and large enough so that the product $\rho\sigma^2$ is of appreciable magnitude (say perhaps $\epsilon\sigma^2 > 0.2$). In this comparatively infrequent special case, j, $j_{min.}$, ϵ and σ can be directly determined from the analysis, provided observations of sufficient accuracy can be made on lines corresponding to the lowest values of j.

Except in cases where there is experimental evidence of a $\rho\sigma^2$ term in ΔF, it has hitherto generally been tacitly assumed that $\sigma=0$. This, however, is evidently unjustified, since if $\rho\sim 0$, the possible presence of a σ in Eq. (8) or (8*A*) would be without effect in Eq. (13) or (14). Thus if T is found to have the values $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, ... one cannot distinguish between the possibilities (1), j=integral, $\rho=\pm\frac{1}{2}$ (either with or without

a *small* σ), and (2), j half-integral, with $\rho=0$, and $\sigma\geqq 0$.—The writer is greatly indebted in this matter to Professor E. C. Kemble, who first brought to his attention the indistinguishability of the ΔF's arising from terms of the forms of Eqs. (8*B*) and (8*C*).

P-, Q-, and R-form branches. Closely related to the question of effective rotational quantum numbers is that of the *form* of the branches of a band. For any band-line, $\nu=\nu^0+B'm'^2-B''m''^2+\ldots$. (cf. Eqs. (2), (3), and (8)). Substituting for $B'm'^2+\ldots$. and $B''m''^2+\ldots$. according to Eq. (8*E*), reducing, and setting $T'-T''=\Delta T$, $\nu^0+B''\sigma''^2-B'\sigma'^2=A$, $B'-B''=C$,and $(\rho'\sigma'^2/j'-\rho''\sigma''^2/j''+\ldots.)=f(j)$, Eq. (15), which is a generalization of Eq. (4), results:

$$\nu=A+B'(\Delta T)^2+2B'T''\Delta T+CT''^2+f(j)+\ldots\ldots \qquad (15)$$

From the definitions of T and ΔT, $\Delta T=\Delta j+(\rho''-\rho')$. Eq. (15) contains the description of all possible branches which can occur by the combination of two terms for which $F(j)$ has the form of Eq. (8).

The simplest case, and the most common in practise, is that in which $\Delta T\sim\Delta j$ and $f(j)\sim 0$, corresponding to $\rho'\sim\rho''$ and $\rho'\sigma'^2\sim\rho''\sigma''^2\sim 0$, as in the violet CN bands ($\epsilon\sim\frac{1}{2}$), the CuH bands ($\rho\sim 0$, $\sigma=0$), or the CO bands ($\rho'=0$, $\sigma'=0$; $\rho''=0$, $\sigma''=1$). In this case the P, Q, and R branches ($\Delta j=-1$, 0, and $+1$, cf. p. 488) take on familiar characteristic forms. But in other cases other forms are assumed, *e.g.*, if $\rho'\sim 0$, $\rho''\sim\pm\frac{1}{2}$, as in the ZnH and analogous bands,[2,10] ΔT has the respective values $+1\frac{1}{2}$, $+\frac{1}{2}$, $+\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{1}{2}$, $-1\frac{1}{2}$, for the R_1, R_2, Q_1, Q_2, P_1 and P_2 branches. Such cases as P or R branches with $\Delta T=0$, or Q branches with $\Delta T=+1$ or -1, are also entirely possible. It is convenient to *define P-form, Q-form, and R-form branches* as branches for which $f(j)\sim 0$ and ΔT has approximately the respective values -1, 0, and $+1$. Branches corresponding to $\Delta T=+2$, $-1\frac{1}{2}$, $+\frac{1}{2}$, etc. (with $f(j)\sim 0$) may be referred to as double-R-form, $1\frac{1}{2}$-P-form, semi-R-form, etc.—In case $f(j)$ is appreciable, the forms of branches are essentially unchanged except for a characteristic deformation (cf. Eq. (15)) for the smallest values of j.

Methods of distinguishing ρ-type and σ-type terms. From the foregoing, it is obviously necessary to find other criteria than the mere form of the empirical ΔF's, or of the observed branches, in order to distinguish between rotational terms of the ρ and σ types (Eqs. (8*B*) and (8*C*)) and the Eq. (8*D*) type. This necessity is also clear from the fact that up to the present all bands not obviously containing terms of the form of Eq. (8*A*) have been tacitly *assumed* to involve only terms of the (8*B*) or (8*D*) form; while according to the present work, many of these same bands have been found to involve terms of the (8*C*) form.

Two valuable aids to decision have been discussed in the two preceding sections. If Q branches are lacking,[21] we can safely[16] rule out the $B(j^2-\sigma^2)$ type in favor of the $B(j-\rho)^2$ type of term. If they are present, we have a strong indication in favor of the $B(j^2-\sigma^2)$ type of term for at least

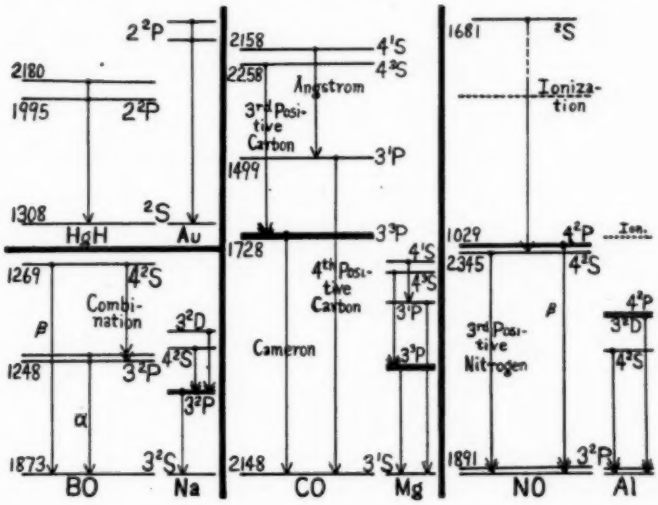


Fig. 1. The energy-levels are all on a uniform scale, except that the doublet separations have been exaggerated ten times in the case of the octet molecules and the correpsonding atoms,—but not in the cases of HgH and Au. The figures in parentheses are vibration frequencies ω_0, expressed in wave-number units, as determined from the band spectra. These give a rough indication of the stability of the molecule for the electronic state in question. At the right are term-designations, including tentative values of the principal quantum number. The energy levels of CO are as given by Birge,[24, 28, 34] complete energy level diagrams of CO, N_2, CO^+, N_2^+, NO, O_2, and O_2^+ are given in a recent article by Birge and Sponer.[34] In regard to BO, cf. ref. 31. The scheme of levels for NO is as determined by Sponer.[34,37] The term-designations are by the writer. The highest level in NO, since it lies above the ionization potential, probably involves simultaneous excitation of two electrons. Denoting by ($3s$, $3s$, $4s$) the individual states of the three outer electrons which give rise to the 4^3S state of NO, this higher state may well be another ^3S state (since experimentally it is single) corresponding to the arrangement ($3s$, $4s$, $4s$). The designation of the NO β bands as $^2P \rightarrow {}^2P$ is a result of recent unpublished work of Dr. F. A. Jenkins, Dr. H. A. Barton, and the writer.

one of the two electronic states. If this is correct, a study of the missing lines yields the value of σ;[22] in fact, the absence of one or more lines

[21] This of course assumes that one can distinguish true Q branches from true P or R branches, regardless of the form; the uncertainties here involved are illustrated in the discussion of the violet CN bands in ref. 11. There is also the difficulty that very short weak Q branches, such as are to be expected in certain cases (cf. discussion in later papers), are likely to be overlooked.

[22] This is strictly true only with the help of the assumption that σ must be either integral or half-integral.

having $T>\frac{1}{2}$, if one can be sure of it, is in itself satisfactory evidence for the presence of a σ.

Since the half-integral or integral character of $T=j-\rho$ can be determined experimentally, it is evident that if we had rules for determining whether j, ρ, and σ should be integral or half-integral for a particular molecule, the ambiguities above brought out might be practically eliminated. Precisely this function is fulfilled by the postulates stated below (p. 503).

Recent Work on the Nature of Electron Levels in Band Spectra

It is natural to suppose that the electronic states of molecules have more or less similarity to those of atoms.[23] Much evidence can be obtained from a study of the electronic frequencies ν^0 (cf. Eq. (3)) alone or with the help of analogies of band-structure between different spectra. The subject has recently been discussed by Birge[24] in an article which gave impetus to the present work.

The first, and very striking, evidence for a parallelism between molecular and atomic electron levels was the discovery of Rydberg series in the spectrum of He_2.[25] There is also evidence of similar series in the H_2 spectrum.[23,26] In the case of other molecules, the evidence is at present slight, although in several cases two or three members of a probable series are known.[24,27,28]

Term-designations. Beyond the establishment of Rydberg series, one might hope to assign definite term-designations and quantum numbers to the electronic states of molecules. After the failure of early attempts at simple molecular models, further efforts were, however, largely held in abeyance.

The first attempt to carry through a systematic analogy between atomic and molecular spectra was made by Mecke.[29] Mecke assumed that the angular momentum of the emitting electron and of the nuclei, in molecules, are respectively analogous, in determining multiplet structure, to the angular momentum of core and of emitting electron in atoms. But Mecke's treatment requires a molecular model[29] which seems

[23] Cf. ref. 4, pp. 92, 734 and 740.

[24] R. T. Birge, Nature, Feb. 27 (1926).

[25] A. Fowler, Proc. Roy. Soc. **91A,** 208 (1915); W. E. Curtis and R. A. Long, Proc. Roy. Soc. **108A,** 513 (1925). Cf. also R. S. Mulliken, Proc. Nat. Acad. Sci. **12,** 158 (1926).

[26] E. E. Witmer, Proc. Nat. Acad. Sci. **12,** 238 (1926).

[27] Excitation potentials of N_2, cf. H. Sponer, Zeits. f. Physik, **34,** 622 (1925).

[28] CO energy levels, R. T. Birge, Nature, Feb. 13 (1926).

[29] R. Mecke, Zeits. f. Physik **28,** 261 (1924) and **31,** 709 (1925).

very improbable for the cases to which he applies it, and is open to serious objection in other ways. The postulates stated below, and the conclusions reached, differ radically from Mecke's, although at some points there is a close superficial resemblance.

Recently evidence was presented by the writer,[30] for a real analogy between the electronic states of certain molecules (BO, CN) and those of the Na atom. These ideas were extended in a later paper which laid some of the foundations for the present work,[31] while additional important evidence has been put forward by Birge, Mecke, and Hulthén. Finally, Birge has postulated a more or less strict and literal analogy between molecular electronic states and certain corresponding atomic states.[24]

The above development has already been reviewed briefly.[1] Some of the results, together with certain new results, are discussed below and in part summarized in Fig. 1. Fig. 1 contains term-designations, including a tentative principal quantum number of the excited electron, for the observed electronic energy levels of three typical "octet molecules"[1] and of HgH, with comparison diagrams of certain comparable atoms. The term-notation is essentially that suggested for use in line spectra in the paper of Russell and Saunders.[32] It is especially important that each diagram in Fig. 1 is *typical* for molecules (neutral or ionized) having the same number of outer electrons. Thus, so far as the data go, the energy levels of CO^+, CN, and N_2^+ (also of SiN and AlO, with eight more electrons) are qualitatively identical[31] with those of BO; those of N_2 are like those of CO[24]; and in O_2^+ there is a system of double-headed ultraviolet bands[33,34,35] which evidently correspond to the β bands of NO. Certain new SiN bands recently described by the writer[36] are probably also of the same type, since in all obvious features they have the same structure as the NOβ and the O^{2+} bands.

Evidence for "octet" structure. The striking parallelism in *nature* (single or double) and *arrangement* of the electron levels in BO, CO, and NO (and their respective homologues) to those of the comparable atoms[24,31] Na, Mg, and Al is evident from Fig. 1. It is on this parallelism that the assigned term-designations and the idea of an "octet" structure for such molecules, plus one, two, or three (3-quantum) outer electrons, are chiefly based. The nature of this structure, and the evidence for it, are further discussed elsewhere.[1,24,31,38]

[30] R. S. Mulliken, Phys. Rev. **25**, 291 (1925).
[31] R. S. Mulliken, Phys. Rev. **26**, 561 (1925).
[32] H. N. Russell and F. A. Saunders, Astrophys. J. **61**, 64 (1925).
[33] R. C. Johnson, Proc. Roy. Soc. **105A**, 683 (1924).
[34] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).
[35] R. Mecke, Zeits. f. Physik. **36**, 795 (1926). The writer is indebted to Dr. Mecke for the opportunity to examine the manuscript before publication.

There is, however, evidence against the "octet" structure and in favor of a molecular model composed of two essentially unchanged atoms whose j_c's interact as seems to be the case in H_2, Na_2, etc.[38] Such a model is indicated by recent evidence of Birge and Sponer,[34] which shows that even such typical octet molecules as CO and NO can probably be dissociated into normal or only slightly excited atoms as the limit of a process of increasing the vibrational quantum number in the normal or one of the excited electronic states of the molecule. Also, Mecke has pointed out[35] that the doublet separations in BO, CO^+ and NO are of the same order of magnitude as the (triplet) separations for the normal state of the O atom, indicating that the emitting electron belongs to the O atom. In the writer's opinion, however, the relations brought out by Mecke are not necessarily incompatible with an octet structure, although the O atom may well exert a dominating influence on account of its relatively great nuclear charge.

Even if the octet idea should prove incorrect, there remains strong evidence, in octet as well as in other molecules (see below), for the existence of multiple electronic states which closely resemble those of atoms.

Other molecules. Aside from octet molecules, evidence has recently been produced from several sources for the existence of ^2P double electronic states. Thus it is likely that the doublet alkaline earth halide bands correspond to the resonance transition $^2P_{1,2} \rightarrow {}^2S$ in the Me^+ ion (*e.g.*, Ca^+) in diatomic molecules Me^+X^- of the one-valence-electron type.[30,39] Mecke has obtained some very interesting quantitative correlations between the observed doublet separations and those of certain corresponding atoms in ^2P states.[40]

The existence of a pair of excited P states in ZnH, CdH, and HgH, related to the P levels of Zn, Cd, and Hg, was first brought out by Hulthén, who supposed the two levels to be $^3P_1$ and $^3P_2$.[41] They have been interpreted as ^2P levels by Mecke[35] and the writer[2]; the doublet separations are close to those of the preceding monovalent atoms Cu, Ag, Au (cf. Fig. 1). Similar relations hold in the alkaline earth halides[40] and in SnCl.[42]

[34] R. S. Mulliken, Phys. Rev. **26**, 319 (1935); new bands, p. 334.

[37] H. Sponer, Nature, Jan. 16, 1926); H. Sponer and J. J. Hopfield, Phys. Rev. **27**, 640A (1926).

[38] R. S. Mulliken, Proc. Nat. Acad. Sci. **12**, 338 (1926).

[39] R. S. Mulliken, Phys. Rev. **26**, 31 (1925).

[40] R. Mecke, Naturwissenschaften, Sept. 4, 1925.

[41] E. Hulthén, Nature, October 31, 1925.

[42] W. Jevons, Proc. Roy. Soc. **110A**, 365 (1926).

An interesting further example occurs in a pair of band-systems described by Jevons, and due to SnCl.[42] Qualitatively, these show exactly the same relations (ω_0 greater for initial state, final electron level double, etc.) as for the $^2S \rightarrow {}^2P_{1,2}$ bands of NO. These bands are then probably due to the transition $^2S \rightarrow {}^2P_{1,2}$ in the Sn^+ ion in a Sn^+Cl^- molecule. The observed doublet separation $\Delta\nu$ is about the same as that of the normal state of the In atom which, like Al and NO, has three outer electrons, and which has the same total number of electrons as Sn^+.

Inapplicability of the azimuthal selection principle. In the cases of BO (cf. Fig. 1) and CO^+ there exist observed *intercombinatons of three electron levels*, and for at least one of these it would seem that there must be a definite failure to obey the azimuthal quantum selection principle of line spectra, *no matter what term-designations* (*including primed terms*) might be substituted for those given.[43]

Preliminary Correlation of Band-Structure and Electronic States in Typical Band Spectra

In earlier sections the influence on band-structure of the quantities ρ and σ has been discussed. Various ambiguities in their experimental determination and criteria for overcoming these, have also been pointed out. It is now natural to try to correlate the evidence from band-structure with the results reviewed in the preceding section, in order to determine finally the real values of ρ and σ and to find how these correspond to *S*, *P*, *D*, etc., electronic states. Such a correlation is expressed in the three postulates stated in the next section and in various conclusions reached with their help. In the present section the postulates will be made plausible by a consideration of typical band spectra, and later will be tested and justified by application to a large number of other spectra. In connection with the present section, reference to the statement of the postulates (p. 503) may be helpful.

Spectra containing terms of the $B(j-\rho)^2$ and Bj^2 types; comparison and interpretation of CuH, HCl, *and violet* CN *band-types.* As has been hinted more than once already, Kratzer's interpretation of the violet CN bands comes near to being the key to the entire situation. It is very instructive

[43] The following facts should, however, be noted: the BO combination bands (Fig. 1) are notably weak (R. S. Mulliken, Phys. Rev. **25**, 284 and 291, 1925); and the CO^+ combination bands, while rather intense at high pressure, at low pressure become very weak compared with the other two systems (F. Baldet, Comptes Rendus **180**, 1201, 1925). It therefore seems possible that these "combination" bands occur only through a violation of the selection principle favored by external electric fields or the proximity of other molecules, and that the other two systems (Fig. 1) are "regular;" this was in fact the writer's original idea (Phys. Rev. l.c., p. 291) in regard to the BO combination bands.

to compare these bands with the electronic bands[29,44,45] of CuH and the infra-red oscillation-rotation bands of HCl. All three sets of bands are superficially almost identical in structure. All have P-form and R-form branches only, which we may without much risk assume to be real P and R branches (cf. ref. 11 on violet CN bands); we can then conclude[16] (cf. p. 498) that $\sigma'=\sigma''=0$ for all. All have half-integral values of T' and T'' (cf. p. 491-2), and in all $T'_{min.}=T''_{min.}=\frac{1}{2}$, since the only evidence of missing lines is in each case a single gap in the series at the null-line. But the lines of the violet CN bands consist of doublets, while those of the CuH bands, and, so far as is known, of the HCl bands, are single.[46,47] The existence and importance of this difference were first emphasized by Mecke.[29]

Analogous to Eqs. (7) and (11) for the violet CN bands, the following equations, which will be introduced here for convenience of later reference, may be expected to hold for the CuH and HCl bands, the only difference being that we are dealing here with single terms:

$$R(j)=F'(j+1)-F''(j)\,; \qquad P(j)=F'(j-1)-F''(j) \tag{16}$$

$$\Delta_2F'(j)=R(j)-P(j)\,; \qquad \Delta_2F''(j)=R(j-1)-P(j+1) \tag{17}$$

As already noted in an earlier section, Kratzer *assumed* integral j values for the violet CN bands, and then found that the observed doublets could be explained by setting $\rho'\sim\rho''\sim\pm\frac{1}{2}$. If integral j values are again assumed for HCl[15] and CuH, one again concludes $\epsilon'=\epsilon''=\frac{1}{2}$; but since the lines are single, only one sign of ρ can be used: either $\rho=+\frac{1}{2}$ or $\rho=-\frac{1}{2}$ seems admissible.[48] Except for the unexplained singleness of the lines, this explanation at first sight seems satisfactory.

But there is a difference between CN and the other two molecules which, if all these molecules were atoms, would be of fundamental importance: CN contains an odd number of electrons, while CuH and HCl each contain an even number. For atoms, this difference would involve a corresponding shift between integral and half-integral values of the inner quantum number j. Of course we may dismiss the matter with the

[44] CuH bands: R. Frerichs, Zeits. f. Physik **20**, 170 (1923); E. Bengttson, Zeits. f. Physik **20**, 229 (1923); absorption of CuH, AgH, AuH, and AlH bands, E. Hulthén and R. V. Zumstein, Phys. Rev. **28**, 13 (1926).

[45] Isotope effect in CuH bands, cf. R. S. Mulliken, Nature **113**, 489 (1924).

[46] In the case of HCl, there is, however, no real experimental evidence against the presence of unresolved narrow doublets.

[47] The direct evidence is very strong that the CuH lines are strictly single (except for a doubling due to isotopy).[29,45] Birge finds (Phys. Rev. **27**, 245A, 1926) that the T' (but not the T'') values depart quite appreciably from half-integers. This is enough practically to insure that doublets, if present, would be resolved.

[48] If one arbitrarily excludes $j=0$, with Kratzer, the case $\rho=-\frac{1}{2}$ is not in accord with observation, since it would give three central missing lines.

remark that molecules do not necessarily behave like atoms; but it seems more reasonable, in the absence of evidence to the contrary, to suppose that they *do* in such respects behave like atoms.

Furthermore, it is generally admitted that the HCl molecule must have an electron shell like that of the argon atom, while, as we have seen in the preceding section, there are strong reasons for believing that the CN molecule[49] has a single valence electron which gives rise to energy levels like those of a Na atom. Now in the HCl bands we are unquestionably dealing with the normal electronic state of the HCl molecule, which should then be a ^1S state like the normal state of argon. This conclusion is further supported by the fact that HCl, like argon, is diamagnetic. In the case of CN, as we have seen, there is strong evidence that the electron levels concerned in the emission of the violet CN bands are both ^2S levels. The lower of these is in all probability[49] the normal state of the molecule, the ^2S level here corresponding to that of the normal state of the Na atom. For a ^2S state $j=\frac{1}{2}$ according to Sommerfeld, $J=1$ according to Landé; for a ^1S state, $j=0$, $J=\frac{1}{2}$.

Everything now fits into place in a most significant way if we suppose that Sommerfeld's atomic j values are the correct j_e values (cf. p. 487) for molecules in corresponding electronic states. The adoption of $j'_e = j''_e = \rho' = \rho'' = \pm\frac{1}{2}$ (in agreement of course with Kratzer) for the violet CN bands, and $j'_e = j''_e = 0$ for the CuH and HCl bands, explains at once the double character of the P and R branches for CN, and their single character in the latter cases. Landé's J values, requiring $\rho = \pm 1$ for the violet CN bands, $\rho = \frac{1}{2}$ for the CuH and HCl bands, would not explain this difference, although apparently capable of explaining the other observed relations.

A consequence of the above interpretation is that for HCl and CuH, the j values are half-integral, while for CN they are integral. This can be seen from Eqs. (8D) and (14); since j_e, ρ, and σ are zero for CuH and HCl, we have $j = m = T = \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \ldots$, for both initial and final electronic states. Denoting integers by τ, half-integers by τ^*, the results may be summarized thus: HCl, HCu, $(j_e, m, j) = (\tau, \tau^*, \tau^*)$; CN, $= (\tau^*, \tau^*, \tau)$.

[49] The direct evidence that the bands are really due to the molecule CN is very strong (cf. R. S. Mulliken, Nature **114**, 838, (1924). The evidence becomes conclusive when the complete analogy[31] of the violet CN bands to corresponding bands of a number of other emitters, in particular N_2^+, is recognized. Similar but slightly less positive statements hold in regard to the evidence that the final state of the violet CN bands is the normal state of the CN molecule; for the N_2^+ bands, the final state has been shown by resonance potential work[27] to be the normal state of N_2, thus showing by analogy that the same in all probability is true for CN.

According to the above interpretations, the absence of the null-line, both in the CN and the CuH bands, is to be explained as discussed on p. 490, and not in agreement with Kratzer. Kratzer's explanation of the missing null-line in the CN bands, as due to the arbitrary exclusion of the state $j=0$ (cf. p. 490), is obviously inapplicable to the CuH bands as here interpreted, since j is half-integral.

According to the above interpretation, the CuH bands correspond to an electronic transition $^1S \rightarrow {}^1S$.[50] As in the case of the $^2S \rightarrow {}^2S$ transitions (violet CN bands) in CN, we must conclude that the emitting electron is not subject to an azimuthal quantum selection principle, and also that the line spectrum prohibition against the change $0 \rightarrow 0$ of j_e is inapplicable here.

The preceding results can be extended to a number of additional band spectra. With the violet CN bands are to be classed the AlO, SiN, N_2^+, BO β, and CO^+ negative Deslandres bands (cf. p. 495); with the CuH bands the analogous AgH and AuH bands (including the new AuH bands of Hulthén and Zumstein[44]); and with the infra-red HCl bands the corresponding HF and HBr bands.

Spectra containing terms of the general Kramers and Pauli type; the CH *bands.* As already noted (p. 492), values of j, ρ, and σ can be determined without assumption in the case of bands involving terms of the form of Eq. (8) with both ϵ and σ of appreciable magnitude. The two CH bands λ3900 and λ4300, as analyzed by Kratzer,[51] have a common final state for which $F(j)$ is clearly of this type, with $\sigma''=1$, $\rho''=\pm\frac{1}{2}$, $j=$integral. The values of $\Delta F(j)$ are, to be sure, not very sensitive to the exact values of σ and j, except for very small j values, but careful examination of all available data, especially for the λ3900 band, indicates that the above values are essentially correct. For the initial states[52] of λ3900 and λ4300, $\sigma=0$, $\rho=\pm\frac{1}{2}$.

The resulting band structure is highly complex but easily recognizable after the analysis into branches has been made. Especially characteristic is the presence of doublets[6] whose separation is small for large values of j but increases rapidly for small j values.[50] In λ 3900 there are two P, two Q, and two R branches, in λ4300 there are four branches of each kind.

[50] The possibility that one or both of the electronic states are $^1P_0$,—which like ^1S has $j_e=0$,—can safely be dismissed because if it were true there should also be $^1P_1$ and perhaps $^1P_2$ combinations.

[51] A. Kratzer, Zeits. f. Physik **23**, 298 (1924).

[52] For the *initial* state of the λ4300 band, Kratzer has tentatively concluded $\sigma=\frac{1}{2}$, $\rho=\pm\frac{1}{2}$, but both the writer and Professor R. T. Birge independently have become convinced that this result is incorrect and that actually $\sigma'=0$. For the initial state of λ3900, Kratzer's conclusion $\sigma=0$, $\rho=\pm\frac{1}{2}$, cannot be criticized.

The above results are important in a number of ways. (1) They show that the general Kratzer-Kramers and Pauli rotational term of Eq. (8) actually occurs in practise,[53] and that a σ really can exist; the presence of this σ, furthermore, accounts for the presence of the observed Q branches (cf. p. 488). (2) They confirm the assumption of integral j values for CH and therefore probably for all odd molecules. (3) They give evidence that a ρ can exist and have the values $\pm\frac{1}{2}$, and thus give support to Kratzer's interpretation of the violet CN bands. (4) The observed ϵ and σ values can reasonably be interpreted as $\sigma=1=j_e$ for the carbon atom, $\epsilon=\frac{1}{2}=j_e$ for the hydrogen atom; the fact that $\sqrt{\epsilon^2+\sigma^2}=1.12$ is neither an integer nor a half-integer is evidence that in the CH molecule there is no resultant molecular j_e, but that instead there are two uncombined atomic j_e's.[54] The value 1 (of σ) is exactly Sommerfeld's j_e for a carbon atom in a ^1P state, (probably not $^3P^1$). The value $j_e=\frac{1}{2}$ is exactly what Sommerfeld's j_e would be for the normal state of the H atom *if it acted like an alkali metal* atom, and may be considered evidence that it does act in this way; this result is in line with recent work of several writers.[55] (5) The evidence stated in (4) for Sommerfeld's j_e values gives support to their applicability in the cases of CN, CuH, HCl, and analogous molecules, and therefore (as will be seen by an examination of the discussion of these spectra) to the m and j values there deduced; the evidence of (2) also supports the j values for CN and its analogues.

Band types having rotational terms of the form $B(j^2-\sigma^2)$: CO *Angstrom bands.* In a recent paper[2] it was shown that the ZnH, CdH, and HgH bands can be more adequately interpreted than heretofore if their initial states involve rotational terms essentially of the form $B(j^2-\sigma^2)$, as in Eq. (8C). A simpler example will now be considered.

The visible CO bands ($^1S\rightarrow{}^1P$ transition in Fig. 1) of Angstrom and Thalén, as recently analyzed by Hulthén,[56] appear to be of the simplest possible type. They contain one P and one R branch, and have $T'=T''$

[53] The objection might be raised that the CH bands constitute an isolated case and that the agreement with the theoretical form is fortuitous, since in the closely analogous OH bands the agreement with the simple formula is only qualitative. But the peculiarities of the OH bands can be explained fairly simply by the assumption of a σ and ϵ which vary systematically with j, a circumstance which may be attributed to an appreciable departure from the rigid fixation of j_e which is assumed by Kramers and Pauli in deducing Eq. (8).

[54] Of course if $\sigma=\sqrt{\frac{3}{4}}=0.87$, we should have $\sqrt{\epsilon^2+\sigma^2}=1$, and it is barely possible that $\sigma=0.87$ is within the limits of error.

[55] S. Goudsmit and G. E. Uhlenbeck, Physica **5**, 266 (1925); J. C. Slater, Proc. Nat. Acad. Sci., Dec., 1924; A. Sommerfeld and A. Unsöld, Zeits. f. Physik **36**, 259 (1926).

[56] E. Hulthén, Ann. der Physik **71**, 41 (1923); Dissertation Lund, 1923. Cf. also Mlle. O. Jasse, Comptes Rendus **182**, 692 (1926).

=half-integral, exactly as in the CuH bands, but in addition possess a Q branch.

The following assumptions are now very natural: (*a*) CO, being an even molecule, has half-integral j values like CuH and HCl; (*b*) the initial state of the Angstrom bands has $j_e=0$ like the ^1S (initial and final) electronic states of CuH and HCl; (*c*) the final state of the Angstrom bands has $j_e=1$, corresponding to Sommerfeld's j for a ^1P state, and this appears in the form $\sigma=1$, $\rho=0$. A little consideration shows that these assumptions are in complete accord with the observed T values, and also account for the presence of the Q branch. According to assumptions (*b*) and (*c*), the initial rotational term is of the simple form $F'(j)=Bj^2$, the final term of the form $F''(j)=B''(j^2-\sigma^2)=B''(j^2-1)$; and in *both* cases (cf. Eqs. (12) and (13)) Δ_1F is of the form $\Delta_1F=2B(j+\frac{1}{2})$. In agreement with this, taking into account assumption (*a*), the empirical ΔF's are both of the form $\Delta_1F=2B\tau$ (τ = integral).

The above assumptions involve very definite requirements as to missing lines (cf. p. 488–89), and thus permit a critical test of their correctness. Since $F'(j)=Bj^2$, we may expect j' to have the values $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, . . .; but for j'' we can expect only $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$, ... , since $F''(j)=B(j^2-1)$. The first possible lines in the P, Q, and R branches, respectively, should then correspond to the following transitions ($j'\rightarrow j''$): $P(\frac{1}{2}\rightarrow 1\frac{1}{2})$, $Q(1\frac{1}{2}\rightarrow 1\frac{1}{2})$, $R(2\frac{1}{2}\rightarrow 1\frac{1}{2})$. The lines $Q(\frac{1}{2}\rightarrow\frac{1}{2})$ and $R(1\frac{1}{2}\rightarrow\frac{1}{2})$, the latter of which is present in HCl and CuH, should thus be cut out. The above-predicted lines are *precisely the observed* first lines[57] recorded by Hulthén.[58]

For convenience of later reference, equations analogous to Eqs. (7) and (11) for the violet CN bands and to Eqs. (18) and (19) for the HCl and CuH bands are given here[59]; the equations for Δ_2F' and Δ_2F'' would be exactly as in Eq. (17), so are not repeated:

$$R(j)=F'(j+1)-F''(j)\,; \qquad (18)$$

$$Q(j)=F'(j)-F''(j)\,; \quad P(j)=F'(j-1)-F''(j)$$

$$\Delta_1F'(j)=R(j)-Q(j)=Q(j+1)-P(j+1) \qquad (19)$$

$$\Delta_1F''(j)=R(j)-Q(j+1)=Q(j)-P(j+1)$$

[57] In Hulthén's notation these are $P(2)$, $Q(2)$ and $R(2)$.

[58] Except that in two out of four bands an additional R line is not recorded, having perhaps been overlooked on account of low intensity. Another interpretation of these bands accounting for the observed missing lines has been given by Kratzer[6], using integral j values and $\epsilon=\frac{1}{2}$. But this interpretation is decidedly forced, and is furthermore inapplicable to the closely related AlH bands (cf. II of this series).

[59] By analogy with the AlH bands which will be discussed in the following paper of this series, it is, however, probable that there are really two values of $F''(j)$ for each value of j'', so that there is really a latent doubling in the lines of the CO bands, but two small to be resolved experimentally, probably on account of the high stability of the molecule. If this is the case, Eqs. (19) and (20) are not strictly correct.

Statement and Critical Discussion of the Postulates and Their Implications, and Summary of Results of their Application

Statement of postulates. With but slight generalization, the leading assumptions and conclusions of the preceding sections can be stated in the form of three postulates; these will be given in slightly different form than in an earlier paper.[1] In the postulates there is of course much that is not novel,—but of which full use is being made for the first time.

I. The electronic states of molecules can be characterized, in accord with Birge's recent postulate,[1,24] by a term-designation (such as ^1S or ^2P, in the notation of Russell and Saunders[32]) carrying implications similar to those for an atom; in particular, this is associated with an electronic quantum number j_e whose numerical value is identical (at least substantially) with *Sommerfeld's* atomic inner quantum number j for the given term-type; or in some cases each atom individually may possess a j_e, and in such cases the electronic states of the H atom are to be classed with those of an alkali metal.

II. The vector or vectors j_e set themselves parallel (ρ components) or perpendicular (σ components), or nearly so, to the vector m, and the rotational energy term is given in the general case substantially by a Kratzer-Kramers and Pauli formula (Eq. (8)).

III. The molecular j has integral values for odd molecules and half-integral values for even molecules, and is subject to the selection principle $\Delta j = 0, \pm 1$, the relative intensities for these three transitions being governed by the correspondence principle.

Remarks on the evidence for the postulates. In the interpretation of any individual band spectrum, there are always various possibilities, the number of these depending on how much of a theoretical nature one assumes. For example, Kratzer's interpretation of the violet CN bands as here adopted, is by no means the only one for which considerable justification can be found.[11] Nevertheless, it gives an explanation of the observed structure, including the doublets, which is *at least* as simple and plausible as any that has been suggested. Similar statements are applicable to the interpretations of other band spectra given in the preceding section.

In most cases, the explanation given has, in the writer's opinion, the maximum of simplicity consistent with the observed degree of complexity of the experimental facts. E.g., in CuH and HCl, the interpretation adopted ($\epsilon' = \epsilon'' = \sigma' = \sigma'' = 0$) is in effect that of the simple rotator (with half-integral rotational quantum numbers). In the case of CO, the necessity of departing a step from this simplest interpretation, in

spite of the very simple arrangement of the branches, is definitely shown by the falling out of a line near the origin which is *present* in the cases of CuH and HCl. This new feature is accounted for by the new assumption $\sigma''=1$ instead of $\sigma''=0$. Again in the CH bands, it is difficult to see how a simpler interpretation of the observed relations could be devised.

In view of these facts, it must surely be significant that all these simple interpretations can be generalized into three plausible and simple postulates (so simple that their power is not at once evident); and that from these postulates all the above interpretations can be deduced at once, together with many more covering most of the band spectra whose empirical structure is sufficiently known. One of the great merits of the postulates is that they make very definite specifications, which render them freely open to experimental test. In this connection it is especially significant that no cases have yet been found which involve a certain contradiction of the postulates.

It should be stated that it appears to be impossible to obtain any consistent agreement with observation if any other systematic choice of j_e and j values is made than that embodied in the postulates as stated.

In spite of the above facts, it is very unlikely that the statement of the postulates given above represents anything final and complete. Formally and empirically, at least, it seems probable, however, that they represent a correct first approximation in ordinary cases at least.

Postulate I and the nature of molecular electronic states; relation of magnetic susceptibilities to electronic states. In spite of postulate *I*, important differences apparently exist between atomic and molecular electron states, as would indeed be expected. Thus molecular *S* states differ (cf. p. 491 and p. 500) from atomic *S* states in that their intercombination is not restricted, even in simple cases, by the azimuthal or inner quantum selection principles of line spectra. Likewise, *P-P* combinations occur.

Nevertheless, the similarity of any molecular electronic state to a corresponding atomic state may be supposed, until contradictions are found, to extend to such quantities as total quantum numbers, Landé *g* factors, and magnetic moments.

From this principle one may conclude, for all diamagnetic diatomic gases (H_2, CO, N_2, halogens, halogen halides, etc.) that $j_e=0$; a similar conclusion doubtless also applies to polyatomic gases. Further, at least in the case of gases whose molecules contain atoms of low atomic weight, we can interpret this as due to a ^1S normal state; for if the lowest excited state were of any other type, such as $^3P_0$, having $j_e=0$, an appreciable fraction of the molecules would be in paramagnetic slightly excited states,

e.g., $^3P_1$ and $^3P_2$ in the case cited. This conclusion is supported by the band spectrum data in cases (CO, HCl) where data are available.

All odd molecules should, from the above principle, be paramagnetic, but such molecules are very rare in the gaseous state, on account of their chemical activity. The most familiar example is NO, whose normal state is apparently a mixture of paramagnetic $^2P_1$ and $^2P_2$ molecules (cf. Fig. 1). The paramagnetism of O_2 shows that its normal state cannot have $j_e=0$. The observed susceptibility is in very close agreement, according to calculations of Sommerfeld,[60] with that of an atom in an S state having $j_e=1$, i.e., a ^3S state. The fact that Curie's law is obeyed to low temperatures for oxygen[61] is strong evidence that only one type of O_2 molecule is present, not e.g., a mixture such as $^3P_0$, $^3P_1$, and $^3P_2$. The ultraviolet oxygen bands also give evidence, although not conclusive, in favor of a ^3S molecular state. But if the indicated correlation is correct, it involves the very surprising and hardly credible result that the O_2 molecule is oriented in a magnetic field in the same way as a ^3S atom, without regard to the rotational motion of the nuclei; for this assumption was involved in Sommerfeld's calculation.

Molecular and atomic j values. From the close analogy which has been shown to exist between molecular electronic states and corresponding atomic states, it seems altogether probable that the definite conclusions reached (and embodied in postulate *I*) as to j_e values in molecules apply directly to the j values of corresponding states of atoms.

Assuming this to be true, $j(=j_e)$ (cf. p. 487) is integral for even atoms and half integral for odd atoms, as supposed by Sommerfeld. But for molecules, according to postulate *III*, $j(\neq j_e)$ is half-integral for even diatomic molecules, and integral for odd diatomic molecules, as if Landé's J values were applicable here. This curious shift is illustrated by considering the process of adding a proton to a Cl^- ion. In the process, $j_e=j=0$ for the Cl^- ion is replaced by $j(\neq j_e)=\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \ldots$ for the molecule.

Other applications of the postulates. The results of the application of the postulates to known band spectra have an important bearing on the problems of molecular structure and molecule formation. The subject has been discussed briefly in previous papers,[2,38] and will be further discussed in connection with later papers.

The application of the postulates gives a new aid to decision in determining the emitter of a band spectrum.

[60] A. Sommerfeld, Atombau, 4th Ed. p. 637–41.

[61] Kammerlingh-Onnes and Perrier, Leiden Comm. 139d, p. 49, ref. 1.

The postulates necessitate a revised interpretation in cases where in the past quarter-integral quantum numbers have been assumed (He_2, cf. R. S. M., ref. 25; HgH, cf. ref. 2; etc.); essentially[62] only integers and half-integers are now used.[63]

Note added to proof.—According to the new quantum mechanics, the term Bj^2 in the expression for $F(j)$ should be replaced by $B(j+\frac{1}{2})^2$, or the latter plus a small constant. This has been shown in detail[64] only for the case $j_e=0$ (Eq. (8*D*) above), but presumably holds in general.[65] If so, and the new mechanics is correct, the true j values are all $\frac{1}{2}$ unit lower than was concluded above (the words "integral" and "half-integral" should then be interchanged in postulate *III*), and the "curious shift" just discussed under "molecular and atomic j values" disappears. Observed intensity relations (at least in bands of the HCl type) are also accounted for more simply than before. Kratzer's seemingly arbitrary exclusion of the state "$j=0$" (cf. p. 490) is now justified, and the absence of the null-line,[64,65] in the violet CN band-type is immediately accounted for by the fact that "$j=0$" would now become $j=-\frac{1}{2}$, which seems meaningless (or else necessarily identical with $j=+\frac{1}{2}$); the occurrence of "$j=0$" in the CH and OH bands (cf. p. 490) seems, however, to conflict with these results.

In a recent important paper,[65] Hund has discussed the interpretation of the phenomena of electronic multiplicity and of fine structure in band spectra. Hund's theoretical deductions have a close relation to the more empirical results of the present series of papers. The subject will probably be further treated later.

In conclusion, the writer wishes to express his appreciation of the valuable suggestions and criticism of Professor E. C. Kemble and Professor R. T. Birge.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
June 15, 1926

[62] This qualification is to take account of the usual small deviations of j_e from an exact integer or half-integer.[1]

[63] The only apparent outstanding exception is CaH band described by the writer (Phys. Rev. **25**, 509 (1925).

[64] L. Mensing, Zeits. f. Physik **36**, 814 (1926); I. Tamm, Zeits. f. Physik **37**, 685 (1926); E. Fues, Ann. der Physik **12**, 367 (1926).

[65] F. Hund, Zeits. f. Physik **36**, 657 (1926).

EXPERIMENTS ON THE SCATTERING OF ELECTRONS BY IONIZED MERCURY VAPOR

By Arthur F. Dittmer

Abstract

Further experimental studies were made of a phenomenon first described by Langmuir. He found that if electrons from a hot filament were projected into an ionized gas with a uniform velocity, they did not retain this uniform velocity but some were retarded and some accelerated as though a random velocity distribution had been impressed upon the uniformally moving stream. The pressure of gas was sufficiently low that only a small percentage of the electrons scattered had collided with gas atoms. Experiments were carried out to determine the exact nature of this scattering and its dependence upon the variables of the tube. The experiments on the variation with distance showed that the scattering all took place within a limited region surrounding the filament, the size of this region being directly proportional to the original velocity of the electrons. With this experimental basis a theory to account for the scattering is indicated. Fluctuations in potential distribution rapid enough to be comparable in period with the time taken by the electrons to pass across the space between the filament and the electrode used to study the velocity distribution are shown to be sufficient to account qualitatively for all the phenomena observed. No direct evidence that these fluctuations are actually present could be obtained. Reasons are given to show that they might be expected. Other possible explanations given by Langmuir have involved new ideas concerning the interchange of energy between either radiation or excited atoms and electrons which seem improbable and which are not required in the explanation here given.

IN a recent article[1] Langmuir has described experiments which show that when a stream of electrons from a hot filament is projected into ionized Hg vapor with a given velocity it is scattered in some manner by the ionized gas, in such a way that some of the electrons have acquired a considerable increment in velocity while a comparable number have been retarded by approximately the same amount. Since the publication of that article the writer has done a considerable amount of experimental work toward finding a cause of this phenomenon, both at the Research Laboratory of the General Electric Company and at the Palmer Physical Laboratory, Princeton, N. J. Some of this work has given results practically identical with those given by Langmuir, some is new, and some appears to disagree with them. It is proposed in the present paper to discuss the problem in the light of these further experimental results and to show their bearing upon any explanation for the phenomenon.

[1] Langmuir, Phys. Rev. **26**, 585 (1925).

A typical experimental tube used in this work is shown in Fig. 1. G is a spherical bulb of Pyrex glass. In most of the work a bulb 20 cms in diameter was used. F is a 7.5 mill W filament about 10 cms in length stretched along a diameter of the bulb and kept taut by the spiral spring S. A and A' are nickel disks about 5 cms in diameter with a hole in the center through which the filament lead passes. They are connected together and form the anode of the tube. C is shown in detail and consists of a nickel disk about 0.5 cm in diameter placed on the end of a glass

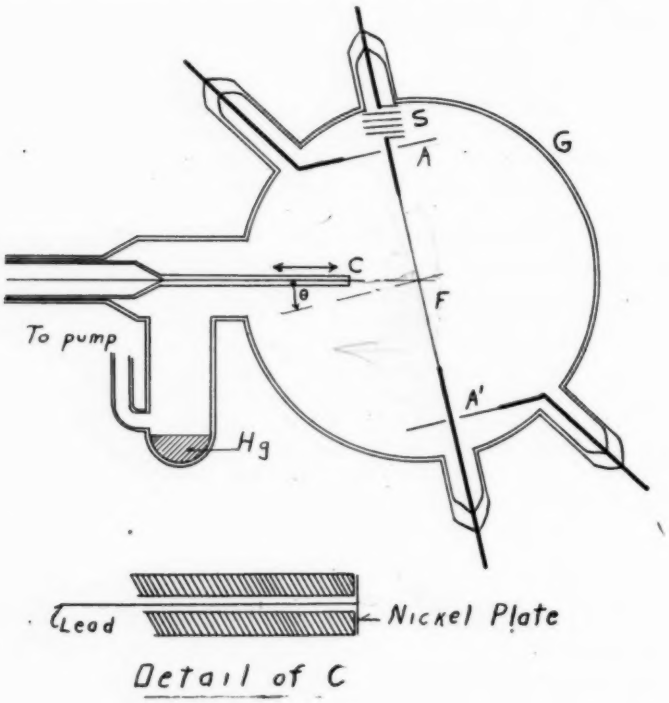


Fig. 1

capillary with an insulated lead as shown. It is constructed so that it can be moved, parallel to itself, along a diameter inclined to the filament at an angle θ, whose significance will be given later, by a magnetic control on a small piece of iron attached to the glass tube supporting C.

Before use the tube is connected to a Hg diffusion pump and a vacuum oil pump in series. It was baked out under high vacuum at about 450°C for a few hours, after which the nickel parts were heated to redness by an induction furnace. After this treatment and with the pumps running the vacuum, while the tube was in use, was always sufficiently good that a sensitive McLeod gauge showed no appreciable pressure. Hg was distilled

in vacuum into the side tube shown and this tube then immersed in a water bath to control the pressure of the vapor, other parts of the tube being always kept at a somewhat higher temperature.

When the filament is heated to a temperature sufficient to emit 100 milli-amperes and a potential of 50 volts is applied between its negative end and the anodes AA' the whole tube is filled with a uniform blue glow. Under these conditions, with a pressure of Hg vapor equal to about 1 bar, the work of Langmuir has shown that conditions in the tube are as follows. The gas in the tube becomes uniformly ionized throughout, the variation in concentration of either positive ions or electrons being not more than 10 or 15 percent between any two points in the bulb. The concentration of positive ions and of free electrons is of the order of 10^{10} per cm^3. Except for small regions surrounding the electrodes and covering the walls and other insulated surfaces in the tube, the whole gas is at very nearly a uniform potential, this potential being near to that of the anode. Its value with respect to the anode, never more than a few volts, is determined largely by the area of the anode. If the anode is very large there is usually a small negative anode drop or the gas is somewhat positive with respect to the anode. With a small anode there is a positive anode drop, the gas being somewhat negative with respect to it. In this work the anodes were of such size that the potential of the gas was always very near to the potential of the anode. The potential drop between the other electrodes and the gas is concentrated in a small region surrounding them. Langmuir calls these regions sheaths. The thickness of these sheaths may be computed from the equation of space charge limited currents between electrodes of the appropriate geometrical form. In especially designed tubes they are visible as dark spaces. With the high ionization present in the tubes where scattering takes place the space charge sheaths are never more than a few tenths of a millimeter in thickness.

Fig. 2 shows the distribution of potential between the filament F and the collecting electrode C under the conditions stated above. The electrons which are emitted from F are accelerated to a velocity equivalent to 50 volts in the sheath surrounding F. The electrostatic field alone would give them velocities strictly normal to F but the magnetic field due to the heating current through F causes them to be deflected from the normal. The magnitude of this deflection can be computed from equations given in a paper by A. W. Hull.[2] The deflection for the particular case of the tube shown in Fig. 1 was computed and the angle θ

[2] Hull, Phys. Rev. **25**, 645 (1925).

shown there given such a magnitude that the closest approximation to normal incidence upon C was obtained. After leaving the filament the electrons move toward the walls of the tube with a uniform velocity until they lose energy or have their direction changed. With Hg vapor at a pressure of 1 bar the mean free path of an electron is about 30 cms. Hence most of the electrons will reach the walls of the tube without colliding with anything. The current to the collecting electrode C at any potential below that of the gas will be made up of a positive ion current and an electron current consisting of those electrons which have components of velocity in a direction normal to C equal to or greater than the velocity necessary to pass against a retarding field equal to the potential of C below that of the gas. In Fig. 2, if C is at the potential given by the point a, it receives only positive ions. When at point b, if the filament F were strictly equipotential, the electrons had no initial velocity of emission, and no scattering took place, it would receive this

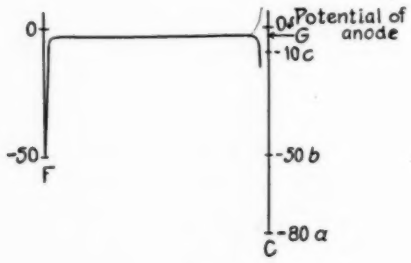


Fig. 2.

positive ion current and that fraction of the electrons emitted by the filament directed toward C, i.e., the fraction given by (Area of C)$/2\pi rl$ where r is the distance of C from F and l is the length of F, which had not suffered loss of energy or deflection in passing through the space between F and C. Langmuir calls these electrons primary electrons. At potentials between b and c, C will receive, in addition to the primary electrons, those which have lost some energy by collision, those which have been somewhat deflected from their original path, and those which are reflected from the walls of the tube but still retain a high velocity. At potentials between c and G the current to C increases rapidly because of those electrons which are present in the gas with small initial velocities. In the present paper only the primary electrons are discussed.

When only a small current, e.g., 10 m.a., is sent through the tube these primary electrons are practically homogenous in velocity and reach the electrode C when it is at the potential of the filament. When the

current is increased it is found that these electrons have been acted upon in some manner so that they no longer have a uniform velocity, but instead some of them have acquired velocity while a corresponding number have lost velocity. In particular, electrons begin to reach the electrode *C* when it is at a considerable negative potential with respect to the filament. This effect is so large that electrons originally accelerated through a 50 volt drop in potential have been observed to reach electrode *C* when it was 40 volts below the filament. As many as 5 percent of the whole number directed toward *C* are able to reach it when it is 25 volts negative with respect to the filament.

It is important to stop and consider just what this means. It means that some of the electrons which leave the filament are able to reach an electrode which is 25 volts or more negative after they have passed a distance of a few centimeters through the ionized gas. These electrons have not collided with gas molecules and hence certainly not with excited molecules so that their energy could not be increased by collisions of the second kind unless one wants to make the assumption that the target area for collisions of the second kind is very much larger than the target area of an unexcited molecule. None of the work on collisions of the second kind would justify any such assumption. The experimental fact is not at all dependent upon any assumption regarding the potential distribution between the filament and the collecting electrode such as is given in Fig. 2. With any distribution whatever the electrons could never reach an electrode more negative than the filament unless they acquire the extra energy somewhere in the space between.

In order to explain this increase in energy three courses seem to be open. First, the increase in energy may be only apparent because of the presence in the circuits of oscillations of such nature that the collecting electrode is at a positive potential with respect to the filament part of the time even when the direct current instruments show it to be 25 volts negative with respect to it. Second, there may be some entirely new mechanism by which the electrons acquire the additional energy. Under this may be included the possible large increase in the target area of excited molecules such that collisions of the second kind are much more frequent than collisions with unexcited molecules and the presence in the space through which the high velocity electrons are passing of a very high energy and temperature radiation from which the electrons are acquiring random energy. This second hypothesis has been discussed in considerable detail by Langmuir.[1] Third, the scattering may be due to a fluctuating distribution of potential between the filament and the collecting electrode. It is

this third hypothesis which the experiments to be described in this paper seem to support.

With regard to the first hypothesis it may be noted that all experiments carried out to detect the presence of oscillations in the external circuit have given negative results. Langmuir[1] states that observations with radio receivers capable of detecting oscillations of 0.5 meter wave-length have shown no oscillations present. The writer using the Braun tube oscillograph and the so-called triode peak-voltmeter has failed to detect any oscillations in the circuits. With these results in mind, together with the fact that tubes in which oscillations are present do not show anything resembling scattering, this first hypothesis may be discarded as not in agreement with experiment.

Before taking up the other two possible causes of the scattering, the main experimental facts regarding it will be given. Some of these are given in Langmuir's paper, while some are the results of experiments carried out since then. It will be convenient to discuss these facts under two general heads. First, the exact nature of the velocity distribution of the electrons after scattering; and, second, the relation of this scattering to the variables in the tube, under which will be included current density, voltage applied or velocity of the primary beam, the pressure of gas in the tube, the geometry of the tube, and the distance the electrons have passed through the ionized gas.

Velocity distribution of electrons after scattering. One fact concerning the scattering is fairly well established. When scattering takes place there is no sharply defined upper limit to the velocity in the beam. In other words, the curve giving the number of electrons or current against the retarding voltage approaches the zero axis asymptotically as the retarding voltage is increased. Some other questions regarding the scattering remain. Among these are the following. Is there any decrease in energy of the beam as a whole and if so is there a general relationship between the retardation and the amount of scattering, amount of scattering being given by one of the parameters discussed below? Is the scattering symmetrical about the average velocity of all the electrons leaving the filament? And is there any simple velocity distribution, i.e., representable by a mathematical formula, which when impressed upon the initial uniform velcity, will give the observed distribution? Many experiments were undertaken to answer these questions, but the inherent experimental difficulties are such that no certain answers can be given. Three difficulties stand out. There is a lack of homogeneity of emission along the filament since the thermionic current is an appreciable fraction of the heating

current through the filament. This cannot be overcome by using large filaments since then the magnetic deflections by the heating current would become very large. The effect of the magnetic deflections due to the heating current through the filament is only very approximately known. No information whatever is available concerning the reflection of electrons from a metal surface covered with a positive ion sheath. Bearing the above sources of experimental error in mind, the following statements concerning the nature of the velocity distribution after scattering based upon over one hundred separate distribution curves may be made. There is some retardation of the beam as a whole but this retardation of the beam bears no general relationship to the amount of scattering. The question regarding the symmetry of the scattering cannot be answered at all. The presence of reflected electrons from the walls of the tube, electrons which have lost some energy, and the wholly unknown factor due to reflection from the collecting electrode form sufficiently large sources of error that practically no significance may be attached to the interpretation of that part of the volt-ampere characteristic of the collecting electrode taken with the electrode positive with respect to the filament. When the logarithm of the current to the collecting electrode is plotted against the retarding voltage a fair agreement with a straight line is obtained in most cases. When the currents are plotted on probability paper according to the method given by Langmuir about equally good agreement with a straight line relationship is obtained. Langmuir has shown that a straight line relationship on probability paper would result if the actual distribution of velocities were made up of a Maxwell distribution in all directions superposed upon the uniform translational motion. The straight line relationship between the logarithm of the current and the voltage corresponds to no simple distribution superposed upon the motion of translation. In general neither of these methods of plotting give any better approximation to a linear relationship when applied to a single distribution curve than they would with any curve drawn at random leaving the zero axis asymptotically and having its convex side downward. Either method of plotting gives a convenient parameter to define the amount of scattering. The agreement of either one with the experimental facts is not sufficiently exact that they need be considered as a necessary consequence of any theory regarding the cause of the scattering. In the discussion of the variation of scattering with the variables in the tube given below, the slope of the best straight line drawn through the points giving the logarithm of the current against the voltage is taken as a measure of the scattering. With no scattering this slope is such that the current increases by ten fold

within less than one volt. With wide scattering the voltage interval for a ten fold increase may become as large as twenty-five volts. In this discussion no numerical values of the scattering are included since the actual values obtained are so dependent upon the geometry of the particular tube used that they are without significance as such.

Variation of scattering with current density. When the current from the filament of a tube such as is shown in Fig. 1 is less than 10 m.a. no scattering takes place. As the current is increased above 10 m.a. the scattering increases rapidly until the current is about 100 m.a. Above this value the rate of increase falls off rapidly as though the scattering were approaching a saturation value. It never becomes quite constant but the change from a current of about 200 m.a. to the highest emission which can be obtained without burning out the filament, about 1 ampere in this particular tube, is very small. The magnitude of this saturation value of the scattering depends upon the velocity of the primary beam and upon the geometry of the tube. The form of the curve giving the change in scattering with current from the filament in a particular tube depends upon the pressure of gas in the tube.

Variation of scattering with velocity of primary beam. As the velocity of the primary beam is increased the maximum scattering which can be obtained is decreased. Experiments with different tubes on the effect of increasing the velocity of the beam show only this in common. The actual form of the variation of scattering with velocity is very different when different tubes are used. Not enough data are available at the present time to say anything definite about the form of this curve.

Variation of scattering with pressure. When the pressure of the gas in the tube is increased the scattering approaches the same saturation value as with the lower pressure but the rate of approach is increased. That is, the current necessary to obtain a given scattering, less than the maximum scattering obtainable in the particular tube used, decreases as the pressure of the gas in the tube is increased.

Variation of scattering with geometry of tube. Only two generalizations concerning the variation of the scattering with the geometry of the tube can be made. The scattering depends upon the emission per unit length of the filament rather than upon the total current through the tube. In particular a tube with a filament 5 cms in length will give approximately the same scattering as a tube with a filament 10 cms in length when the current through the former is one-half that through the latter. The maximum scattering which can be obtained in a tube is a function of the volume of the tube. The maximum scattering obtainable decreases as

the volume is increased. Sufficient data are not available to show any definite relationship.

None of the above variations of scattering with the variables in the tube seem to give any definite information about its cause, other than that the general results given above would have to be considered in formulating a theory. The variation of the scattering with the distance traversed by the electrons seemed to offer the best means of studying the effect. A series of experiments are carried out to study this variation. These will now be described in some detail. In a footnote Langmuir has described an experiment using a tube with two filaments placed very close together which shows that the scattering does not take place within a region very close to the filament.

The tube shown in Fig. 1 was used. The side tube containing Hg was immersed in melting ice so that the pressure of Hg vapor was .23 bars. At this low pressure the mean free path is of the order of a meter thus making correction for the number of electrons lost by collisions as the distance was increased unnecessary. The thermionic current used was 500 m.a. since previous experiments had shown that with this current the scattering had reached almost a constant saturation value. Volt-ampere characteristics of C were taken at intervals of 0.5 cm from 1 cm to 8 cms distance. The currents obtained were separated into positive ion and electron currents by extrapolation of the curve obtained for high negative voltages when only positive ions were received. The electron currents at any given distance were multiplied by this distance to correct for the change with distance of the number of electrons directed toward *C* from the filament. These corrected electron currents were then plotted against the retarding voltage as shown in Figs. 3 and 4. The curve at the left in each figure gives the electron currents at one cm distance from about 18 volts below the filament to 2 volts above. Accurately stated it gives the currents from 10 volts below the negative end to 10 volts above. The actual potential of that point on the filament from which the electrons reaching *C* came could be found only approximately by taking a volt-ampere characteristic with no scattering. It was found to be about 8 volts more positive than the negative end. After plotting the curve for one cm the voltage scale was shifted a convenient distance to the right and the curve for 1.5 cms plotted. The same procedure was carried out for the rest of the distance. The curves drawn across the figure then give the manner in which the number of electrons which have gained a certain amount of energy varies with the distance. These curves are drawn for every 2 volts between 10 volts below and 10 volts above the negative end of the filament. They show conclusively that the scattering takes

place within a distance of a few cms of the filament and then remains constant. Fig. 3 is for electrons initially accelerated to a velocity equivalent to approximately 20 volts. The scattering remains constant beyond

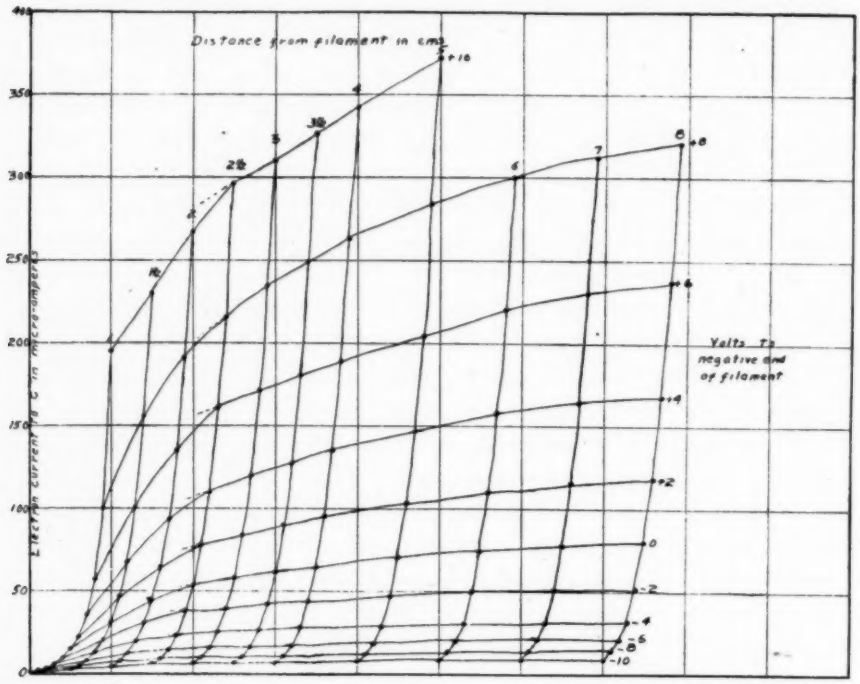


Fig. 3.

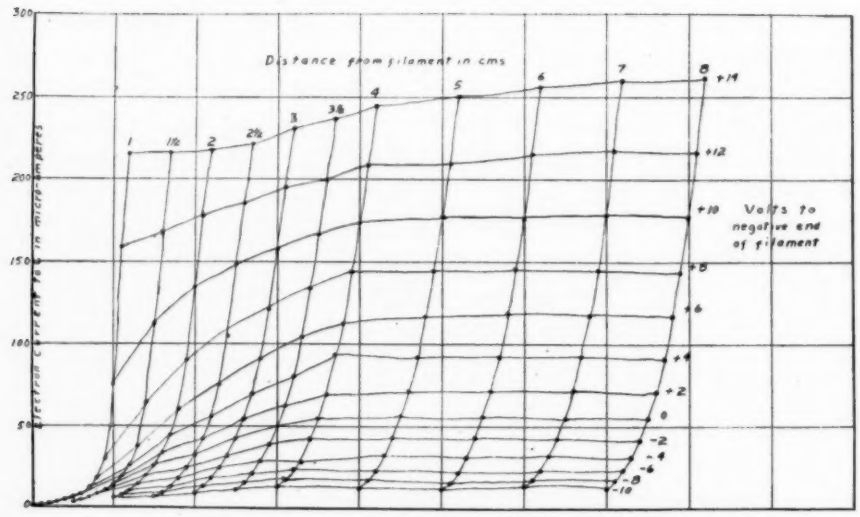


Fig. 4.

a distance of 2.5 cms. Fig. 4 is for electrons accelerated initially to a velocity equivalent to about 40 volts and here the scattering does not remain constant until a distance of 4 cms is reached. Plots like Figs. 3 and 4 were made for electrons of velocities between 20 and 100 volts at 20 volt intervals and these confirm the conclusion that the distance in which the scattering reaches a constant value is proportional to the square root of the voltage or to the velocity of the electrons which are scattered. Experiments were also carried out in a tube in which the variation of scattering with distance was studied out to a distance of 26 cms from the filament. This tube could not be made symmetrical about the filament as is the tube shown in Fig. 1 and hence the correction for the number of electrons directed toward *C* as the distance increased could not be accurately made. But the results obtained showed that the scattering remained constant beyond a distance of 3 or 4 cms from the filament.

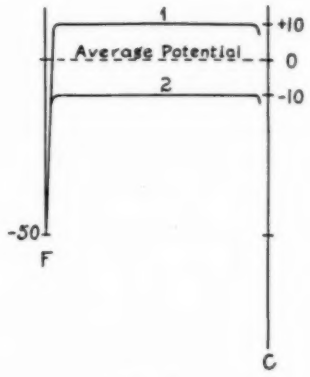


Fig. 5.

These experiments show definitely that the scattering is not due to any mechanism by which the electrons acquire random energy from the ionized gas. If it were due to any such mechanism the scattering should increase steadily with the distance, the rate of increase varying perhaps inversely with the distance since the concentration of fast moving electrons varies inversely as the distance from the filament.

All the phenomena described above may be at least qualitatively accounted for if the assumption is made that the potential distribution between the filament and the collecting electrode does not remain as shown in Fig. 2 but instead fluctuates rapidly between two distributions such as are given in Fig. 5. This figure is drawn merely to illustrate the argument and is not intended to represent the actual state of affairs. If this fluctuation is rapid enough so that its period is comparable with

the time required by an electron to pass across the space, then electrons could reach C when it was at a lower negative potential than F. Suppose, for example, that an electron left the filament while the distribution was that given by curve 1. It would be accelerated to a velocity equivalent to 60 volts. If while moving across the space the distribution changed to that given by curve 2 the electron would still have a velocity equivalent to 60 volts and could reach C when that electrode was at a potential 20 volts negative with respect to the filament. The fact that the scattering reaches a constant value in a distance which is proportional to the speed of the electrons lends some support to such an assumption. If these fluctuations in space charge were periodic some periodicity in the variation of scattering with distance should be observed. No such effect could be detected. Hence it must be concluded that they are aperiodic in character. As stated above electrons of velocity equivalent to 20 volts were scattered differently up to a distance of 2.5 cms from the filament. From this some idea of the rapidity of the fluctuations necessary to account for the scattering may be obtained since they would have to occur in a time less than the time taken by these electrons to move 2.5 cms. Since the velocity of an electron after dropping through a potential of 20 volts is about 3×10^{8} cms per second this time would be of the order of 10^{-8} seconds. In other words they would be comparable in rapidity with radio waves whose wave-length is of the order of 300 cms. This is just the same order of magnitude as the oscillations found in tubes showing the Barkhausen Kurz effect.[3]

Attempts by the writer to account for such variations have been without result. This is not surprising since no adequate explanation has ever been given of just why the potential distribution should be that given in Fig. 2 which is the result of experiment. Just one observation might be given. In Fig. 6 let A and A' be the position of parallel plane electrodes, A giving off electrons so as to form a cathode. Curve 2 gives the distribution of potential when no charge is present between the plates. Curve 1 gives a possible distribution of potential when only electrons are present in the space between. Curve 3 gives a possible distribution of potential when an ionized gas is present between the electrodes. The area between 1 and 2 is some function of the amount of negative electricity between the plates. Similarly, the area between 2 and 3 is some function of the amount of positive electricity between the plates. When an ionized gas is present in the tube the amount of electricity necessary to change the distribution from 3 to 1 is always a very small fraction of the amount

[3] Barkhausen and Kurz, Phys. Zeits. **21**, 1 (1920); Gill and Morrill, Phil. Mag. **44**, 161 (1922).

carried either by the positive ions or the free electrons in the space. This means that very small changes in the ratio of the two could produce very wide variations in the potential distribution. Something similar to this must occur in a tube such as shown in Fig. 1 to account for fluctuations in potential distribution. Very small disturbances in the balance between the concentration of positive ions and of electrons could thus produce wide variations. The fact that much larger scattering is always observed in small tubes than in large ones could be accounted for on this basis. If the fluctuations are due to variations in the rate at which a number of electrons equivalent in the mean to the current given off by the cathode leave the space through which the primary electrons are passing then the same variations in a small tube as in a large tube would give a wider fluctuation in potential in the small tube since the ratio of the concentrations would be altered most in a small tube.

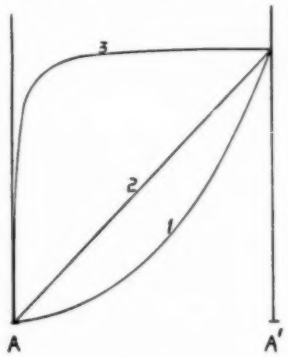


Fig. 6.

One experimental fact is very difficult to reconcile with any theory of the scattering. If conditions in the tube are such that the primary electrons are distributed over a range of 30 volts, about 90% of the slow moving electrons in the gas, whose concentration is about 1000 times that of the primaries, still have a velocity distribution covering a range of only 4 or 5 volts at the most. It is difficult to see how any mechanism could alter the velocity of a fast moving electron by as much as 15 volts while leaving 1000 practically stationary electrons, which are present in the same space, practically unaltered in velocity. But this difficulty is no greater in the theory advanced in this paper than in any theory based upon an equilibrium with either radiation or excited atoms or both.

Attempts were made to show that such variations in the space potential are actually present. No method was devised which gave further information. The best method of study would probably be a modification of the

methods used to study the "shot" effect[4] in electrons from a hot filament. The special apparatus necessary to do this was not available to the writer. Such experiments should show definitely if such variations in the potential of the space really were present and the writer hopes to carry them out at some future time.

In conclusion the writer wishes to express his indebtedness to Dr. Irving Langmuir under whom work in this problem was first begun and to Professor K. T. Compton under whose direction the work has been carried on at Princeton.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
PRINCETON, NEW JERSEY,
May 20, 1926.

[4] Hull and Williams, Phys. Rev. **25**, 147 (1925).

VARIATION WITH TEMPERATURE OF THE WORK FUNCTION OF OXIDE-COATED PLATINUM

By Myron S. Glass

Abstract

A series of tests was made with standard Western Electric VT2 vacuum tubes, in which the filament was held at a higher temperature for a period of five minutes and then returned to a lower reading temperature (950°C) and the electron current measured with a plate potential of 110 volts. It was found that the previous heating of the filament caused a temporary increase in the electron current over the normal value for that temperature, and that this effect increased with temperature up to about 1130°C, after which point it began to fall off. The results of another series of tests indicate that positive ion emission from the filament begins at a temperature somewhat above that which produced maximum electron current. These results are in agreement with the theory that the thermionic activity of oxide-coated platinum filaments is probably due to a film of metallic barium and strontium produced by reduction of the oxides.

THE results of experiments performed by Langmuir and Kingdon,[1] Ives,[2] and Killian,[3] seem to indicate that the decrease in the work function of hot tungsten in the presence of the vapors of the alkali metals, or when thorium oxide is present as an impurity in the tungsten, is due to the formation of a film of those metals on the surface of the tungsten. In the work leading up to the present paper, similar experiments have been tried with platinum filaments coated with the oxides of barium and strontium.

The electron current in a standard Western Electric VT2 tube with 110 volts between filament and plate-grid was measured over a range of "activating" temperatures from 950°*C* to 1200°*C*. By "activating" temperature is meant the temperature at which the filament was held for a period of five minutes previous to the taking of the reading. All the readings were actually taken at the temperature of 950°*C*. In this way, the relative amounts of activation produced at different temperatures could be shown without subjecting the filament to the injurious effect of heavy plate current at high temperatures. Since the emission from these filaments has been shown to obey Richardson's equation, we may attribute any change in the emission produced by the heating to changes in the work function.

[1] Langmuir and Kingdon, Science **57,** 58 (1923); Proc. of Roy. Soc. **107,** Jan. 1, 1925

[2] Ives, J. of Franklin Inst. Jan., 1926.

[3] Killian, Phys. Rev. **27,** 578 (1926).

The method of manipulation was as follows: The filament was brought up to reading temperature (950°*C*) and held at that point until the plate current became constant. The plate voltage was then turned off and the filament was maintained at the activating temperature for a period of five minutes, then returned to reading temperature. The plate current was found to be higher then before, but if allowed to stand for a few minutes (five to ten minutes) it would come back to the normal value. As soon as it became constant again the process was repeated for another temperature. By this means it was found that the electron emission increased with "activating" temperature up to approximately 1100°*C* as measured by an optical pyrometer. Beyond that point the plate current began to fall off with further increase in temperature.

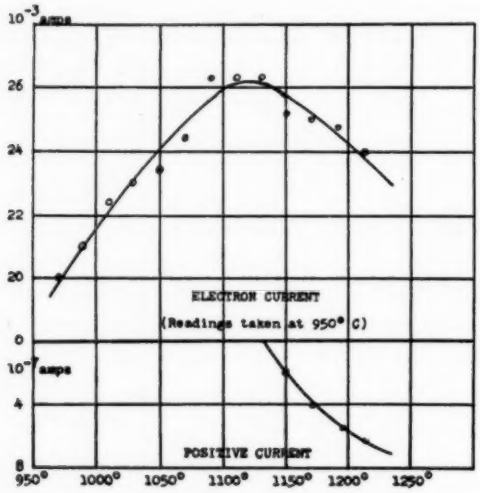


Fig. 1.

A series of tests was then made to determine whether any production of positive ions occurred at various temperatures. Some difficulty was experienced in this because of the fact that in a vacuum tube which has had some use a very thin film of metal may distill over from the filament onto the insulation and cause a slight leakage between filament and plate. A tube was selected in which this effect was not noticeable, and a set of readings for the positive and negative emissions were taken immediately after each other. The results of this experiment are shown in the graph. It will be noticed that the maximum electron emission occurred for an "activating" temperature of about 1120°*C*. This value is preferable to that obtained in the first series because of refinements introduced in the

method of temperature measurement. It will be noticed further that positive ion emission began slightly above 1130°C.

These results are in agreement with the theory that the activity of the oxide-coated platinum filament is probably due to a film of metallic barium and strontium produced by reduction of the oxides, just as the activity of tungsten filaments varies with the coating of alkali metals. The extent of this chemical change apparently depends upon the temperature of the filament, and the amount of metallic film present at any temperature represents the equilibrium condition between formation and evaporation at that temperature. At low temperatures the metal evaporates as neutral atoms, but as the rate of evaporation begins to exceed the rate of production, a part of the filament may be left without a coating of the metal and its work function is higher than the ionizing potential of the escaping atoms. When this condition is produced some of the evaporating electrons will be deprived of one electron, and they then appear as positive ions. Similar considerations have been applied by Langmuir and Kingdon, and Ives to the emission of positive caesium ions from tungsten.

In conclusion, I wish to express my indebtedness to Dr. A. J. Dempster for helpful suggestions pertaining to all phases of the work, and to Dr. M. J. Kelly of the Bell Telephone Laboratories for the tubes used in the experiment.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
June 15, 1926.

SECONDARY EMISSION FROM METALS DUE TO BOMBARDMENT OF HIGH SPEED POSITIVE IONS

By W. J. Jackson

Abstract

A beam of K^+ ions from the iron catalyst source discovered by Kunsman was collected in a Faraday cylinder. A target could be interposed at the mouth of the cylinder by a magnetic control. The difference in current measured in these two cases gave the amount of secondary emission. A transverse magnetic field could be applied at the target to prevent emission of electrons and thus separate electron emission from positive ion reflection. The percentage secondary emission due to bombardment of positive ions having speeds up to 1000 volts has been found for three metals; viz., aluminum, nickel, and molybdenum under a variety of surface conditions. Heat treatment in general reduced the secondary electron emission. The secondary electron emission could not be detected (was less than 0.5%) at positive ion velocities less than 200 volts for Al, 300 volts for Ni, and 600 volts for Mo after heat treatment. The secondary emission increased from these values to 7.0% for Al, 4.2% for Ni, and 3.8% for Mo at 1000 volts. Without heat treatment the emission was detected at lower voltages and reached about double the above values at 1000 volts. The secondary electrons emitted were of low speed, a retarding field of a fraction of a volt was enough to stop nearly all of them. In the cases of molybdenum and nickel positive ion reflection did not exceed 2%, and was undetectable in the case of aluminum.

Introduction

MANY investigators have undertaken the measurement of electron emission from metallic surfaces due to the bombardment of positive ions, but the results obtained have not been in agreement. The purpose of the present work is the measurement of the emission from various metals by using different kinds and speeds of positive ions and by following a method the results of which will be unequivocal. We have endeavored to separate the phenomenon of positive ion reflection from electron emission, a matter which has not received much attention on the part of many workers in the field.

Among the early workers on this problem was Villard,[1] who found that cathode rays are formed by positive ions impinging on the cathode. A few years later J. J. Thomson[2] found that when alpha rays from polonium bombarded a metal, many slow speed electrons were emitted.

Füchtbauer[3] has shown that negative rays are given off when a metal is hit by canal rays, and that the velocity of the negative rays is inde-

[1] Villard, Journ. de Phys. **8**, 1 (1899).
[2] Thomson, Proc. Cam. Phil. Soc. **13**, 49 (1904).
[3] Füchtbauer, Phys. Zeit. **7**, 153–157 and 748–750 (1906).

pendent of the velocities of the canal rays. If 30,000 volt canal rays bombard metals in all cases electrons are emitted, aluminum giving three electrons for each canal ray and platinum giving one electron.

In this connection mention should be made of the work on delta rays by Campbell,[4] Bumstead,[5] and McLennan and Found.[6]

Later work by Cheney[7] did not take account of positive ion reflection. He obtained a secondary emission of about 9 percent from aluminum bombarded by 600 volt potassium ions and about 2.5 percent for platinum using the same kind and speed of ions. He says nothing concerning the treatment given the metal surface.

Secondary emission due to canal rays going through thin gold foil was measured by Hahn.[8] He found that the emission grew with increasing speed of the primary particles. A measure of the velocity distribution of the secondary electrons was made and it was found that as the primary ion velocity was increased the proportional number of small velocity electrons was decreased.

Recently, Klein[9] obtained secondary emission from nickel due to bombardment by positive ions having a velocity of 50 volts and this emission increased to 22 percent at 380 volts. Klein interpreted certain of his results as indicating a large percentage of positive ion reflection of low speed positive ions.

Townsend[10] in his theory of ionization by collision does not take account of the part which the electrode material may play. On his theory the sparking potential depends only on the properties of the gas. Holst and Osterhius[11] have developed a theory of sparking potential suggested by a series of experiments on the rare gases in which they discovered an important influence of the material of the cathode in the vicinity of the minimum sparking potential.

Reliable data along the line of the present experiment would aid greatly in deciding between the above theories of the sparking potential of a gas.

Description of Apparatus and Method

Fig. 1 shows the type of apparatus used in this experiment. The filament *F*, a platinum strip coated with the iron catalyst source dis-

[4] Campbell, Phil. Mag. **22,** 276 (1911); **23,** 46 (1912).
[5] Bumstead, Am. Journ. of Sci. **36,** 91–108 (1913).
[6] McLennan and Found, Phil. Mag. **30,** 491 (1915).
[7] Cheney, Phys. Rev. **10,** 335 (1917).
[8] Hahn, Zeits. f. Physik. **14,** 368 (1923).
[9] Klein, Phys. Rev. **26,** 800 (1925).
[10] Townsend, Electricity in Gases, 428 (1915).
[11] Holst and Osterhius, Comptes Rendus **175,** 577 (1922).

covered by Kunsman,[12] emitted a beam of potassium ions when heated to a dull red heat. That the ions emitted from this source were singly charged potassium ions was shown by work done by Barton, Harnwell and Kunsman[13] in this laboratory by the mass spectrograph method.

The ions were accelerated through the system of slits in the molybdenum cylinder *B*, through the hole in the shield *C*, and were collected in the long Faraday cylinder *D*. The experimental tube is drawn to scale, the line in the upper left-hand corner of the figure representing a length of 10 cm. The slits in the cylinders were of such dimensions as to give a well defined beam of ions. The target *T* which was welded to the molybdenum rod *E* and pivoted at *O* could be interposed exactly at the mouth of the cylinder *D*, or withdrawn from the opening, by applying a magnetic field to the iron armature *H*. A nickel cylinder *N* in whose

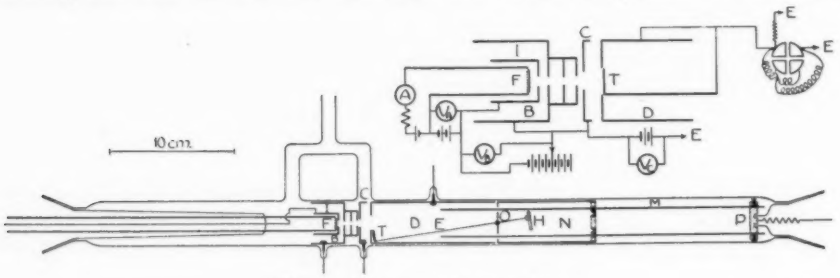


Fig. 1. Diagram of apparatus.

head was a pivot carrying the target, could be made to slide on the tungsten rods *M* by a magnetic control. The target could thus be moved back in the tube a few centimeters from the end of *D* so that it could be heated by induced currents from a high frequency a.c. coil wound around the tube. The rods *M* were mounted through a ground glass joint sealed on the outside by De Khotinsky cement. The filament *F* was mounted similarly through another ground glass stopper.

The apparatus was evacuated by means of a mercury diffusion pump backed by a Cenco Hyvac pump. There were two outlets from the tube so that as good a vacuum as possible might be obtained between *B* and *D* and any gas which might come from the filament was thus rapidly pumped out. Before a series of runs the experimental tube was baked in an electrical furnace at about 400°C. Liquid air was used to keep oil and mercury vapor from the apparatus. During a run with the pumps going the pressure was too small to be detected by a McLeod gauge reading 10^{-6} mm of mercury.

[12] Kunsman, J. of Phys. Chem. **30**, 525–534, April (1926).
[13] Barton, Harnwell and Kunsman, Phys. Rev. **27**, 739 (1926).

The upper right-hand portion of Fig. 1 shows the electrical connections. A constant potential difference V_A of 90 volts supplied by dry cells was applied between the filament F and the iron cylinder I. This cylinder was used to shield the filament magnetically. The accelerating potential V_B was varied from 0 to about 1000 volts. Dry cells supplied this voltage V_B which was measured by a Weston Standard voltmeter having a resistance of one megohm. The currents were measured by the constant deflection method on a Dolazek electrometer with a sensitivity of about 1000 divisions per volt, shunted by India ink resistances. A few turns of fine platinum wire were wrapped around the stem and tube, and connected to earth as guard rings. The whole apparatus was enclosed in an earthed wire cage. With such precautions the possibility of surface leakage of electricity from the outside or electrostatic disturbance was reduced to a minimum.

The difference in the electrometer current in the two positions of the target gave a measure of the secondary emission.

Let I_+ represent the primary positive ion current, I_- the secondary electron current, and I_r the current due to reflected positive ions.

If, when the target is withdrawn, the total current measured is I_1, and when the target is exposed to bombardment the current measured is I_2, we have

$$I_1 = I_+ \text{ and } I_2 = I_+ + I_- - I_r,$$

whence

$$\frac{I_1}{I_2} = \frac{I_+}{I_+ + I_- - I_r},$$

therefore

$$\frac{I_2 - I_1}{I_1} = \frac{I_- - I_r}{I_+}$$

is the ratio of the secondary emission to the primary positive ion current.

Now if a transverse magnetic field be set up which causes the emitted electrons to be curved back upon the target but which is not large enough to affect the positive ions, then

$$\frac{I_1^H - I_2^H}{I_1^H} = \frac{I_r}{I_+}$$

is the ratio of the positive ions reflected to the primary positive ion current, I_1^H and I_2^H being the current measured with the magnetic field applied when the target is back and forward respectively.

An idea of the magnitude of the magnetic field necessary to bend the electrons without affecting the positive ions can be obtained from a

formula given by J. J. Thomson[14] for determining e/m when using a magnetic field to stop ions passing between parallel plates; namely, $e/m = 2V/(Hd)^2$ where e/m is the ratio of the charge to the mass of the ion, V the potential difference between the plates, H the magnetic field, and d the distance between the plates.

Results

(a) *Secondary emission.* In Fig. 2 experimental curves are given in which $(I_2 - I_1)/I_1$ expressed in percent is plotted as ordinate and V the accelerating potential of the positive ions is plotted as abscissa. Curve B is a typical curve for a molybdenum target which had been baked *in vacuo* at about 1000°C, and then exposed to air before final evacuation of the apparatus. Curve B_1 shows the results obtained using the same target after it had been baked *in vacuo* in the experimental tube by induced currents. Curve A shows the results for a molybdenum target which had been baked as before, exposed to a gas flame and then mounted in

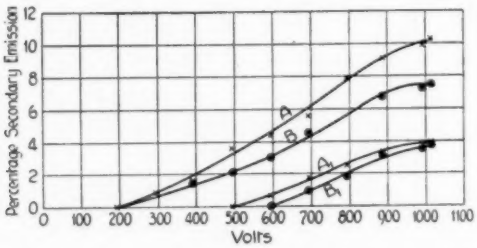


Fig. 2. Percentage of secondary emission as a function of velocity of positive ions.

the tube. Curve A_1 gives the percentage secondary emission for various speeds of the bombarding positive ions, after the target had been baked in the apparatus. It will be noted that the emission depends somewhat on previous treatment of the target.

Fig. 3 shows the emission from three metals, molybdenum, nickel, and aluminum, which had been baked in the experimental tube. Curves are not given to indicate the amount of emission from aluminum and nickel before baking in the apparatus. It will suffice to say that from aluminum an emission of 15 percent to 20 percent was obtained due to the bombardment of 1000 volt positive ions, and in the case of nickel an emission of about 7 percent was measured due to ions of the above speed.

(b) *Positive ion reflection.* In experiments on positive ion reflection a transverse magnetic field was applied at the target. In the case of molybdenum positive ion reflection did not exceed 2 percent for the highest

[14] Thomson, Conduction of Electricity Through Gases, Second Edition, p. 219.

speeds of primary ions used. In working with nickel it was discovered that the magnetic field could not be utilized to separate the effect of positive ion reflection from electron emission owing to the magnetic property of the nickel which weakened the field in the region of emission. However, since it was found that the electrons emitted from nickel had low speeds, nearly all being stopped by a fraction of a volt and none having a speed greater than 3 volts, a retarding field of 3 volts for electrons was applied between *C* and *D* (Fig. 1) and it was then discovered there was not more than 2 percent reflection of positive ions. In the case of aluminum there was no evidence of positive ion reflection.

If a field of 45 volts was applied to retard positive ions between *C* and *D* (Fig. 1), the low speed ions 0 to 2 volts were affected by the field and cases were obtained in which 50 percent fewer ions reached the cylinder *D* when the target was forward than in the case of the target being back. This phenomenon disappeared when the field between *D* and *C* was made small. It is quite evident, therefore, that this is not a phenomenon of

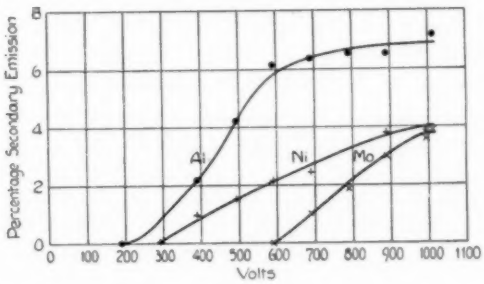


Fig. 3. Percentage of secondary emission as a function of velocity of positive ions.

reflection of low speed positive ions but an effect due to deflection of primary ions by the field. These observations at large retarding fields were exactly similar to those reported by Klein[9] and interpreted by him as indicating positive ion reflection. The present observations show that positive ion reflection is certainly less than 2 percent, and may be zero.

(c) *Velocity of the emitted electrons.* It was found that the electrons emitted from the three metals were of low speed. In the experiments performed practically all could be stopped by retarding fields of a fraction of a volt.

Table I shows the fraction of emitted electrons having speeds less than a certain value for various speeds of bombarding positive ion. The data given in Table I were obtained from a nickel target.

TABLE I

V_Bv	(f)* 0.1v	(f) 0.2v	(f) 0.3v	(f) 0.5v	(f) 1.0v	(f) 2.0v
400	.5	1	1	1	1	1
500	.7	1	1	1	1	1
600	.7	.9	1	1	1	1
700	.7	.85	.93	1	1	1
900	.58	.58	.61	.79	.84	.88

* $f(v)$ means the fraction having speeds less than v volts.

The above table indicates that the velocity distribution among the secondary electrons increases with the speed of the bombarding positive ion.

Discussion of Results

From the curves in Fig. 1 it will be seen that the emission from metallic surfaces due to positive ion bombardment depends on the treatment of the surface. Doubtless much which is measured as electron emission from metals is really emission from layers of gas absorbed on the surface. One feature of the experiment was the baking of the target in the experimental tube by induced currents.

It should be noted as shown in Fig. 3 that secondary emission sets in for aluminum at a lower voltage of bombarding ion than for nickel, and emission from nickel at a lower voltage than from molybdenum. This may be due to aluminum having a lower work function than nickel and nickel having a lower work function than molybdenum.[15] Whether or not this is the explanation will become clearer after more metals have been studied. Perhaps results obtained from aluminum are not comparable with those from nickel and molybdenum as difficulty was encountered in getting the aluminum target baked by induced currents.

This work is being continued with other metals and other kinds of positive ions, in an endeavor to throw more light on the phenomenon of secondary emission from metals. A steady source[12] of positive ions of different kinds being available makes experimentation in this field easier.

In conclusion, the writer wishes to express his thanks to Professor K. T. Compton, at whose suggestion the problem was undertaken, for his kindly interest and helpful counsel during the progress of the work, to Mr. C. C. Van Voorhis who helped in the construction of the apparatus used, and to Mr. Leigh Harris who did the glass work on the experimental tube.

Palmer Physical Laboratory,
Princeton, N. J.
June 1926.

[15] Richardson, Emission of Electricity from Hot Bodies, pp. 81–82.

NEW DEDUCTIONS OF THE ELECTROMAGNETIC EQUATIONS[1]

By W. F. G. Swann

Abstract

Two derivations of the circuital relations are given. *First derivation.* We assume that there exists a vector $\mathbf{E}$ whose divergence $\rho \equiv \text{div } \mathbf{E}$ is conserved in the sense of the equation of continuity

$$\frac{\partial \rho}{\partial t} + \text{div } \rho \mathbf{u} = 0$$

We thus find div $\left(\rho \mathbf{u} + \frac{\partial \mathbf{E}}{\partial t}\right) = 0$ so that there exists a vector $\mathbf{H}$ such that

$$\rho \mathbf{u} + \frac{\partial \mathbf{E}}{\partial t} = c \text{ curl } \mathbf{H}$$

We complete our specification of $\mathbf{H}$ by the assignment of a quantity σ, and define div $\mathbf{H}$ as div $\mathbf{H} \equiv \sigma$. The assumption that σ is conserved in the sense of the equation of continuity leads to the conclusion that there exists a vector ϵ such that

$$-\left(\sigma \mathbf{v} + \frac{\partial \mathbf{H}}{\partial t}\right) = c \text{ curl } \epsilon$$

If we then postulate that the whole system of equations is invariant in form under the Lorentzian transformation, we deduce that $\epsilon = \mathbf{E}$, and the equations assume the classical form generalized by the σ terms. The association of the vectors which appear in the transformed system with those in the untransformed system is discussed, and is shown to require, logically, a specification of the nature of the definition of $\mathbf{E}$. It is shown that if $\mathbf{E}$ be defined in terms of the motion produced in an electron, the rigorous establishment of the correspondence necessitates the assumption of a suitable equation of motion.

Second derivation: We assume an equation of electronic motion of the form

$$\mathbf{E} + \frac{[\mathbf{wH}]}{c} = \mathbf{P}$$

where $\mathbf{P}$ is a function of the motion of the electron such that $k\mathbf{P}$, $ki\ (\mathbf{P}.\mathbf{w})/c$ is a 4-vector, and $k = (1 - w^2/c^2)^{-\frac{1}{2}}$, and where $\mathbf{E}$ is defined as the limit of $\mathbf{P}$ when $\mathbf{w}$ is zero, and $\mathbf{H}$ is defined in terms of the limiting ratio of the absolute magnitude of $\mathbf{P} - \mathbf{E}$ to the absolute magnitude of $\mathbf{w}$. The assumption of the invariance of this equation for a transformation from a system S to a system S' leads to a relation between the fields in the two systems. ρ and σ are defined as div $\mathbf{E}$ and div $\mathbf{H}$ respectively, and it is assumed that, $d\tau$ being an element of volume, $\rho d\tau$ is invariant and $\sigma\, d\tau$ is invariant. It is then shown that the invariance of $\rho \equiv \text{div } \mathbf{E}$ and $\sigma \equiv \text{div } \mathbf{H}$ necessitate respectively,

$$\frac{1}{c}\left(\rho \mathbf{u} + \frac{\partial \mathbf{E}}{\partial t}\right) = \text{curl } \mathbf{H} \text{ and } -\frac{1}{c}\left(\sigma \mathbf{v} + \frac{\partial \mathbf{H}}{\partial t}\right) = \text{curl } \mathbf{E}.$$

[1] The first part of this paper was presented at the American Mathematical Congress at Toronto, August, 1924.

Introduction

THE electromagnetic equations

$$\frac{1}{c}\left(\rho\mathbf{u}+\frac{\partial \mathbf{E}}{\partial t}\right)=\text{curl}\,\mathbf{H} \tag{1}$$

$$\rho=\text{div}\,\mathbf{E} \tag{2}$$

$$-\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t}=\text{curl}\,\mathbf{E} \tag{3}$$

$$\text{div}\,\mathbf{H}=0 \tag{4}$$

have been discussed from many standpoints, both as to their logical origin, and also as to the significance of the vectors occurring in them. Probably the most logical attitude is to regard the equations as definitions of $\mathbf{E}$ and $\mathbf{H}$[2] in terms of quantities ρ and $\mathbf{u}$ which are assigned to the volume element of space in such a way that

$$\frac{\partial \rho}{\partial t}+\text{div}\,\rho\mathbf{u}=0. \tag{5}$$

On such a basis the equations call for no derivation, and the justification for their existence rests on the possibility of assigning to the volume element of space values of ρ and $\mathbf{u}$ satisfying (5) and such that when $\mathbf{E}$ and $\mathbf{H}$ are defined in terms of them the values of $\mathbf{E}$ and $\mathbf{H}$ so defined will be found of service—as for example in expressing the motion of some identifiable singularity such as an electron. As a matter of fact it is in this sense that the equations are actually used whatever else may be in the mind of the user as to the significance of his operations. Nevertheless the process of starting with the quantities $\mathbf{E}$ and $\mathbf{H}$ defined in some other way and then deducing the equations on the basis of some principle which is taken as a starting point is one which has occupied a prominent place in the classical discussions of the subject. As two of this class of "derivations" the following are suggested.

First Derivation

The first derivation exhibits the extent to which the forms of the equations are determined by the vectorial properties of the quantities related as distinct from any mysterious and complicated collocation of experimental facts. The equations will appear in a generalized form permitting the occurrence of magnetic poles, or distributions of positive and negative magnetism. The generalization to include these magnetic

[2] See for example W.F.G. Swann, "The Fundamentals of Electrodynamics," Part I of Bulletin No. 24 of the National Research Council.

charges is, of course, not new, and the primary feature of the paper lies in the simple nature of the assumptions which are:

(a)[3] An assumption which amounts practically to providing for conservation of electric charge and "magnetic charge."

(b) The laws of vector analysis, which are the equivalent of the assumption of invariance of physical laws under a rotation of axes in space.

(c) Invariance of the forms of the laws under the transformation of the restricted theory of relativity.

Let us start by assuming that there exists a vector **E**, defined in some way which it is unnecessary for us to specify, and subject only to the condition that the volume integral of its divergence is conserved in the sense more explicitly implied in the equation of continuity. In other words, we assume that if ρ is defined as

$$\rho \equiv \text{div } \mathbf{E} \text{ (definition of } \rho) \tag{6}$$

there exists a vector **u**, transformable as a velocity under the restricted theory of relativity and such that

$$\text{div } \rho\mathbf{u} + \frac{\partial \rho}{\partial t} = 0 \text{ (assumption)} \tag{7}$$

From (6) and (7) it follows immediately that

$$\text{div}\left(\rho\mathbf{u} + \frac{\partial \mathbf{E}}{\partial t}\right) = 0 \tag{8}$$

Hence, it is possible to choose a vector **H**, such that

$$\rho\mathbf{u} + \frac{\partial \mathbf{E}}{\partial t} = c \text{ curl } \mathbf{H} \tag{9}$$

No generality is lost by the inclusion of the constant c since the value of this constant only affects the unit in which **H** is measured. We shall, in fact, take (9) as our definition of **H**; or, since a vector is not completely defined by its curl, we shall suppose that there exists a quantity σ, which by writing

$$\sigma \equiv \text{div } \mathbf{H} \text{ (definition of div } \mathbf{H}) \tag{10}$$

[3] As a matter of fact, even (a) would be formally unnecessary as regards the conservation of electric charge for a generalized form of the equations in which $\rho\mathbf{u}$ was replaced by a vector **j** which did not necessarily claim expression in the form $\rho\mathbf{u}$. The "spirit" of conservation of charge would still be implied, however, in that the vector **j** would have to be such that $\text{div } \mathbf{j} + \frac{\partial \rho}{\partial t} = 0$.

serves to complete our specification of $\mathbf{H}$.[4] We shall not find it necessary to specify the nature of the definition of σ further than to say that it must transform as a density. In other words, it is to be obtained by specifying for each volume element of space a number (an invariant under the Lorentzian transformation), and then dividing the number by the element of volume. It is unnecessary to specify the method of defining the invariant numbers. Any unsatisfactory feeling resulting from our giving no explicit definition of them vanishes, of course, for the case of classical electrodynamics where they are zero, i.e., where $\operatorname{div}\mathbf{H}=0$.

We suppose that σ, like ρ, is, as regards its volume integral, conserved in the sense of the equation of continuity. In other words, we suppose that associated with each point there exists a velocity $\mathbf{v}$, such that

$$\operatorname{div}\sigma\mathbf{v}+\frac{\partial\sigma}{\partial t}=0 \tag{11}$$

so that, from (10) and (11)

$$\operatorname{div}\left(\sigma\mathbf{v}+\frac{\partial\mathbf{H}}{\partial t}\right)=0 \tag{12}$$

which tells us that a vector $\boldsymbol{\epsilon}$ exists such that

$$\sigma\mathbf{v}+\frac{\partial\mathbf{H}}{\partial t}=-c\operatorname{curl}\boldsymbol{\epsilon} \tag{13}$$

Again, we lose no generality in inserting the constant factor $-c$ since only the unit in which $\boldsymbol{\epsilon}$ is measured is thereby involved.

Collecting our results we have

$$\frac{1}{c}\left(\rho\mathbf{u}+\frac{\partial\mathbf{E}}{\partial t}\right)=\operatorname{curl}\mathbf{H} \tag{14}$$

$$\rho=\operatorname{div}\mathbf{E} \tag{15}$$

$$-\frac{1}{c}\left(\sigma\mathbf{v}+\frac{\partial\mathbf{H}}{\partial t}\right)=\operatorname{curl}\boldsymbol{\epsilon} \tag{16}$$

$$\sigma=\operatorname{div}\mathbf{H} \tag{17}$$

Already we note the similarity to the electromagnetic equations (1)–(4), generalized by the addition of the terms involving σ, and it only remains to show the identity of $\mathbf{E}$ and the $\boldsymbol{\epsilon}$ of equation (16) to convert that similarity into a complete correspondence.

[4] For if $\operatorname{div}\mathbf{H}$ and $\operatorname{curl}\mathbf{H}$ are specified for all points in space, $\mathbf{H}$ is determined at any point, provided that the usual conditions at infinity are satisfied. The definition of $\mathbf{H}$ in this manner is by no means artificial, and corresponds to the sense in which the vector is actually used in electrodynamics.

The criterion imposed by relativity. Let us submit Eqs. (14) and (15) to the transformation

$$x'=\beta(x-vt),\ y'=y,\ z'=z',\ t'=\beta\left(t-\frac{v}{c^2}x\right) \tag{18}$$

$$\text{with } \beta=\left(1-\frac{v^2}{c^2}\right)^{-\frac{1}{2}}$$

which takes them from a system which we shall call S to another designated by S'. From (18)

$$\frac{\partial}{\partial x}=\beta\left(\frac{\partial}{\partial x'}-\frac{v}{c^2}\frac{\partial}{\partial t'}\right),\ \frac{\partial}{\partial y}=\frac{\partial}{\partial y'},\ \frac{\partial}{\partial z}=\frac{\partial}{\partial z'},$$

$$\frac{\partial}{\partial t}=\beta\left(\frac{\partial}{\partial t'}-v\frac{\partial}{\partial x'}\right) \tag{19}$$

also

$$\frac{\partial}{\partial x'}=\beta\left(\frac{\partial}{\partial x}+\frac{v}{c^2}\frac{\partial}{\partial t}\right),\ \frac{\partial}{\partial y'}=\frac{\partial}{\partial y},\ \frac{\partial}{\partial z'}=\frac{\partial}{\partial z},$$

$$\frac{\partial}{\partial t'}=\beta\left(\frac{\partial}{\partial t}+v\frac{\partial}{\partial x}\right) \tag{20}$$

The velocities transform according to the well known relations

$$u_x'=\frac{u_x-v}{1-\frac{u_xv}{c^2}},\quad u_y'=\frac{u_y}{\beta\left(1-\frac{u_xv}{c^2}\right)},\quad u_z'=\frac{u_z}{\beta\left(1-\frac{u_xv}{c^2}\right)} \tag{21}$$

$$v_x'=\frac{v_x-v}{1-\frac{v_xv}{c^2}}\quad v_y'=\frac{v_y}{\beta\left(1-\frac{v_xv}{c^2}\right)}\quad v_z'=\frac{v_z}{\beta\left(1-\frac{v_xv}{c^2}\right)} \tag{22}$$

Proceeding in the usual way, we readily find from (14) and (15)

$$\frac{\rho'\mathbf{u}'}{c}=-\frac{1}{c}\frac{\partial\mathbf{E}'}{\partial t'}+\operatorname{curl}'\mathbf{H}' \tag{23}$$

$$\rho'=\operatorname{div}'\mathbf{E}' \tag{24}$$

where div′ and curl′ refer to operations in terms of the primed variables, and where

$$E_x'=E_x,\quad E_y'=\beta\left(E_y-\frac{v}{c}H_z\right),\ E_z'=\beta\left(E_z+\frac{v}{c}H_y\right) \tag{25}$$

$$H_x'=H_x,\ H_y'=\beta\left(H_y+\frac{v}{c}E_z\right),\quad H_z'=\beta\left(H_z-\frac{v}{c}E_y\right) \tag{26}$$

$$\rho'=\beta\rho\left(1-\frac{u_xv}{c^2}\right) \tag{27}$$

In an exactly similar manner, from Eqs. (16) and (17) we find

$$-\frac{\sigma' \mathbf{v}'}{c} = \frac{1}{c}\frac{\partial \mathbf{H}''}{\partial t'} + \operatorname{curl}' \epsilon' \tag{28}$$

$$\sigma' = \operatorname{div}' \mathbf{H}'' \tag{29}$$

where

$$\epsilon_x' = \epsilon_x, \quad \epsilon_y' = \beta\left(\epsilon_y - \frac{v}{c} H_z\right), \quad \epsilon_z' = \beta\left(\epsilon_z + \frac{v}{c} H_y\right) \tag{30}$$

$$H_x'' = H_x, \quad H_y'' = \beta\left(H_y + \frac{v}{c}\epsilon_z\right), \quad H_z'' = \beta\left(H_z - \frac{v}{c}\epsilon_y\right) \tag{31}$$

$$\sigma' = \beta\sigma\left(1 - \frac{v_x v}{c^2}\right) \tag{32}$$

Now (23) and (24) are of the same form in ρ', $\mathbf{u}'$, $\mathbf{E}'$ and $\mathbf{H}'$ as (14) and (15) are in ρ, $\mathbf{u}$, $\mathbf{E}$, and $\mathbf{H}$; and (28) and (29) are of the same form in σ', $\mathbf{v}'$, ϵ', and $\mathbf{H}''$, as (16) and (17) are in σ, $\mathbf{v}$, ϵ, and $\mathbf{H}$. An exact correspondence in form between (23), (24), (28), (29) and (14), (15), (16), (17) requires that $\mathbf{H}'' = \mathbf{H}'$; and, as may be seen from (26) and (31), this necessitates $\epsilon_y = E_y$, and $\epsilon_z = E_z$. The application of a Lorentzian transformation for a velocity parallel to the y direction would, on the same line of argument lead to $\epsilon_z = E_x$, $\epsilon_z = E_z$. Thus, the requirement that the equations shall revert to the original form as a result of the transformations necessitates that $\epsilon = \mathbf{E}$, so that our original Eqs. (14)–(17) assume the form of classical electrodynamics, generalized by the addition of the terms involving σ. Logical precision demands that we say more about this matter before regarding it as complete, however.

Eq. (24) shows us that the ρ' which occurs in (23) is the quantity defined as $\operatorname{div}' \mathbf{E}'$, so that the definitions of ρ and ρ' correspond in the two systems. Eq. (32) tells us that the σ' of Eqs. (28) and (29) transforms as a density transforms, so that it is the quantity which would be obtained by dividing the invariant number above referred to as associated with any element of volume by the magnitude of the element of volume in the system S'. In other words the definitions of σ and σ' correspond in the two systems. From a logical standpoint, however, it is necessary for us to show that the vectors $\mathbf{E}'$ and $\mathbf{H}'$ really mean to the observer in S' the same things that $\mathbf{E}$ and $\mathbf{H}$ mean to the observer in S. This is a matter which is not emphasized as much as it might be in the classical demonstrations of the invariance of the electromagnetic equations. It requires that we consider the corresponding *definitions* of the electric and magnetic fields in S and S' and prove that, in the sense of these definitions, $\mathbf{E}'$ and $\mathbf{H}'$ correspond to $\mathbf{E}$ and $\mathbf{H}$. Of course, our criterion

of invariance will necessitate that when all is finished the quantity which occupies the position of $\mathbf{H}'$ in (23) shall be the same as the quantity which occupies the position of $\mathbf{H}''$ in (28) and (29), but without further examination we have no right to suppose this quantity to be $\mathbf{H}'$ or $\mathbf{H}''$.

The definition of the electric field as the force on unit charge has no means of realization for sub-molecular dynamics unless that force be measured in terms of some motion associated with it—the motion of an electron, for example. Our first thought is naturally to define the electric field as a quantity proportional to the acceleration of an electron.[5] Realizing that this definition would fit in neither with the ideas of variation of electronic mass with velocity which experience has taught us to retain, nor with the influence of a magnetic field on the electron when the latter is in motion, we are next urged to define $\mathbf{E}$ as proportional to the acceleration of an electron whose velocity is zero. Unfortunately, our familiarity with the whole electrodynamic structure causes us to recall that, in the electronic equation of motion to be finally provided for, all the time derivatives of the electron's velocity may be expected to occur. It would, in general, be impossible for an electron to adjust its motion in the field in which it found itself so as to be consistent with its equation of motion and at the same time show a finite acceleration and zero value for all the higher time derivatives of its motion. If in terms of the field which was ultimately defined the equation of motion involved no higher time derivatives than the acceleration, we could logically define the electric field as proportional to the acceleration when the velocity was zero. There is nothing to prevent our *defining* it in this way whatever the ultimate equation of motion may be. Unless that equation contains no higher derivatives than the acceleration, however, the quantity we so define as the field cannot be expected to have the properties of the field which figures in electrodynamics, or in fact, any simple properties.

In spite of what has been written above, it will be convenient to illustrate the argument to be made in what follows by confining ourself in the first instance to a case where the ultimate equation of motion is free from all time derivatives of the motion higher than the acceleration. It will then be readily possible to extend the ideas to the more general case.

Let us then imagine an electron at rest in the system S, and define the electric field $\mathbf{E}$ as

$$E_x = a\ddot{x}\,;\ E_y = a\ddot{y}\,;\ E_z = a\ddot{z}$$

where a is a constant, and the acceleration is estimated in each case for

[5] We refer of course to the field other than that of the electron itself.

the condition of zero velocity. For the definition of the electric field in the system S' we must concern ourselves with an electron which has zero velocity in that system, and define the field $\mathbf{E}_0'$ as

$$(E_0')_x = a\ddot{x}' \; ; \; (E_0')_y = a\ddot{y}' \; ; \; (E_0')_z = a\ddot{z}'$$

The acceleration of an electron measured in a system S' in which it has zero velocity is related to its acceleration measured in some other system in which it has velocity v parallel to the x axis by the well known relation

$$\ddot{x}' = \beta^3\ddot{x} : \ddot{y}' = \beta^2\ddot{y} \; ; \; \ddot{z}' = \beta^2\ddot{z}$$

so that

$$(E_0')_x = a\beta^3\ddot{x} \; ; \; (E_0')_y = a\beta^2\ddot{y} \; ; \; (E_0')_z = a\beta^2\ddot{z}$$

Thus, the vector $\mathbf{E}'$ defined in (25) will be the same as $\mathbf{E}_0'$, and will represent the field in S' provided that

$$E_x = a\beta^3\ddot{x} \; ; \; E_y - \frac{v}{c}H_z = a\beta\ddot{y} \; ; \; E_z + \frac{v}{c}H_y = a\beta\ddot{z}$$

or, put in vectorial form, provided that

$$\mathbf{E} + \frac{[\mathbf{wH}]}{c} = a\frac{d}{dt}(k\mathbf{w}) \tag{33}$$

where $\mathbf{w}$ represents the vector velocity of the electron, $k = (1 - w^2/c^2)^{-\frac{1}{2}}$, and w is the absolute velocity of the electron.

Thus, with the definition of $\mathbf{E}$ which we have made, it results that the establishment of a correspondence between $\mathbf{E}$ and $\mathbf{E}'$ as representatives of the measured electric fields in S and S' necessitates the assumption of an equation of motion of the electron; and even though the definition of the field in any one system concerns itself only with an electron of zero velocity in that system, the equation of motion which is necessitated by the correspondence of $\mathbf{E}$ and $\mathbf{E}'$ involves the dependence of the acceleration on the velocity for a given field. These considerations apply with equal force to classical demonstrations pertaining to the transformation of the electromagnetic equations, although their full importance does not seem to be emphasized in these demonstrations.

Now having imported an equation of motion into our system of laws, the criterion of relativity imposes the necessity of invariance upon it and, as we shall see, this provides for the correspondence between $\mathbf{H}$ and the $\mathbf{H}'$ of Eq. (26).

It follows as a direct analytical consequence of (33) that

$$(\mathbf{E} \cdot \mathbf{w}) = c^2 a\frac{dk}{dt}$$

Now, as is well known, the four quantities $k\,d(k\mathbf{w})/dt$, kic, constitute a 4-vector. Thus, if $\mathbf{E}_0'$ and $\mathbf{H}_0'$ represent the electric and magnetic fields in S', in the sense of their proper definition, since the criterion of invariance requires that, in S', an equation similar to (33) shall hold, but with $\mathbf{E}$, $\mathbf{H}$, $\mathbf{w}$, k, dt replaced by $\mathbf{E}_0'$, $\mathbf{H}_0'$, $\mathbf{w}'$, k', dt', it is necessary that $k(\mathbf{E}+\frac{[\mathbf{w}\,\mathbf{H}]}{c})$, $ki(\mathbf{E}\cdot\mathbf{w})/c$ shall be related to the corresponding quantities in k', $\mathbf{w}'$, $\mathbf{E}_0'$, and $\mathbf{H}_0'$ by the transformation of a 4-vector. Thus,

$$k'\left\{(E_0')_x+\frac{[\mathbf{w}'\,\mathbf{H}_0']_x}{c}\right\}=\beta k\left\{E_x+\frac{[\mathbf{w}\,\mathbf{H}]_x}{c}-\frac{v}{c^2}(\mathbf{E}\cdot\mathbf{w})\right\} \tag{34}$$

$$k'\left\{(E_0')_y+\frac{[\mathbf{w}'\,\mathbf{H}_0']_y}{c}\right\}=k\left\{E_y+\frac{[\mathbf{w}\,\mathbf{H}]_y}{c}\right\} \tag{35}$$

$$k'\left\{(E_0')_z+\frac{[\mathbf{w}'\,\mathbf{H}_0']_z}{c}\right\}=k\left\{E_z+\frac{[\mathbf{w}\,\mathbf{H}]_z}{c}\right\} \tag{36}$$

$$k'\,(\mathbf{E}_0'\cdot\mathbf{w}')=\beta k\left\{(\mathbf{E}\cdot\mathbf{w})-v\left(E_x+\frac{[\mathbf{w}\mathbf{H}]_x}{c}\right)\right\} \tag{37}$$

Let us consider an electron which has a velocity w_y' parallel to the y' axis in S', w_x' and w_z' being zero. Then $w_x=v$, $w_z=0$, and since $k\mathbf{w}$, kic is a 4-vector,

$$k'=\beta\left(k-\frac{v}{c^2}ku_x\right)=\beta k\left(1-\frac{v^2}{c^2}\right)=\beta^{-1}k \tag{38}$$

Thus, (36) yields

$$k'\left\{(E_0')_z-\frac{w_y'(H_0')_x}{c}\right\}=k\left\{E_z+\frac{w_xH_y-w_yH_x}{c}\right\} \tag{39}$$

Since $w_x=v$, and since we have already provided for the equality of $(E_0')_z$ and $\beta(E_z+\frac{vH_y}{c})$, Eq. (39) leads, in view of (38) to

$$k'w_y'(H_0')_x=kw_yH_x$$

Since, however, $k\mathbf{w}$, kic is a 4-vector, $k'w_y'=kw_y$ so that

$$(H_0')_x=H_x \tag{40}$$

Again, (34) yields

$$k'\left\{(E_0')_x+\frac{w_y'(H_0')_z}{c}\right\}=\beta k\left\{E_x+\frac{w_yH_z}{c}-\frac{v}{c^2}(E_xw_x+E_yw_y)\right\}$$

$$=\beta k\left(1-\frac{v^2}{c^2}\right)E_x+\frac{\beta kw_y}{c}\left(H_z-\frac{v}{c}E_y\right) \tag{41}$$

From (38), $k'=\beta k(1-\frac{v^2}{c^2})$. Since $k\mathbf{w}, kic$ is a 4-vector, $k'w_y'=kw_y$, and since we have provided for the equality of $(E_o')_x$ and $E_x(=E_x')$, Eq. (41) gives

$$(H_0')_z=\beta\left(H_z-\frac{v}{c}E_y\right)=H_z'. \tag{42}$$

Similarly by considering an electron for which $w_y'=w_x'=0$, and applying (34) we find

$$(H_0')_y=\beta\left(H_y+\frac{v}{c}E_z\right)=H_y' \tag{43}$$

Thus the equation of motion which we have been driven to accept in order to make $\mathbf{E}'$ correspond to $\mathbf{E}_o'$, requires by its invariance that $\mathbf{H}_o'=\mathbf{H}'$, and we may now with greater rigor than before take up the argument at the stage reached in Eqs. (6) to (10).

Since, as we have already remarked, Eq. (32) shows that σ' is the true density appropriate to the system S' and since our definition of $\mathrm{div}'\mathbf{H}_o'$ in S' must correspond to that of div $\mathbf{H}$ in S, we must have, since $\mathbf{H}_o'=\mathbf{H}'$,

$$\beta\sigma\left(1-\frac{v_x v}{c^2}\right)=\sigma'=\mathrm{div}'\,\mathbf{H}'$$

Using (26)

$$\beta\sigma\left(1-\frac{v_x v}{c^2}\right)=\frac{\partial H_x}{\partial x'}+\beta\left(\frac{\partial H_y}{\partial y'}+\frac{v}{c}\frac{\partial E_z}{\partial y'}\right)+\beta\left(\frac{\partial H_z}{\partial z'}-\frac{v}{c}\frac{\partial E_y}{\partial z'}\right)$$

so that, in view of (20)

$$\beta\sigma\left(1-\frac{v_x v}{c^2}\right)=\beta\,\mathrm{div}\,H+\frac{\beta v}{c^2}\frac{\partial H_x}{\partial t}+\frac{\beta v}{c}\left(\frac{\partial E_z}{\partial y}-\frac{\partial E_y}{\partial z}\right)$$

Since $\sigma\equiv\mathrm{div}\,\mathbf{H}$

$$-\frac{\sigma v_x}{c}=\frac{1}{c}\frac{\partial H_x}{\partial t}+\frac{\partial E_z}{\partial y}-\frac{\partial E_y}{\partial z}$$

The symmetry of the laws with regard to rotation of axes in space, thus gives immediately

$$-\frac{\sigma\mathbf{v}}{c}-\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}=\mathrm{curl}\,\mathbf{E}$$

which is Eq. (3) generalized by the addition of the term in σ. Thus we have the whole set of Eqs. (1)–(4), generalized by the inclusion of σ.

Our definition of $\mathbf{E}$ in terms of the electronic acceleration for zero velocity has led to an equation of motion (33) which does not involve

higher time derivatives of the motion than the acceleration, so that if this equation of motion were true, there would be no ambiguity in our definition of **E** resulting from failure to make any statement as to the magnitudes of the higher derivatives. If, however, the equation of motion assumed were not true, and if the true equation did involve the higher derivatives, the starting point of our assumptions would have to be that there exists some vector **P** which is a function of the motion, such that $k\mathbf{P}$, $ki(\mathbf{w}\cdot\mathbf{P})/c$ is a 4-vector, and such that if **E** be defined as the value of **P** when **w** is zero, the equation of motion of the electron for all values of **w** is

$$\mathbf{E}+\frac{[\mathbf{wH}]}{c}=\mathbf{P}$$

This is all that is necessary to provide for

$$k\left(\mathbf{E}+\frac{[\mathbf{wH}]}{c}\right),\quad \mathrm{ki}(\mathbf{w}\cdot\mathbf{E})/\mathrm{c}$$

being a 4-vector, and so for the relations

$$(E_0')_x=E_x;\quad (E_0')_y=\beta\left(E_y-\frac{v}{c}H_z\right);\quad (E_0')_z=\beta\left(E_z+\frac{v}{c}H_y\right)$$

$$(H_0')_x=H_x;\quad (H_0')_y=\beta\left(H_y+\frac{v}{c}E_z\right);\quad (H_0')_z=\beta\left(H_z-\frac{v}{c}E_y\right)$$

i.e., $\mathbf{E}_o'=\mathbf{E}'$, and $\mathbf{H}_o'=\mathbf{H}_o$ which relations when taken in conjunction with the assumptions specified in (a) and (b), and with the requirement $\mathrm{div}'\,\mathbf{H}_o'=\sigma'$, carry with them as before the electrodynamic Eqs. (1)–(4) generalized by the addition of the σ terms.

Second Derivation

In this derivation we shall proceed on the basis that both **E** and **H** are defined in terms of the motion of an electron.

The definition of **H** as the force on a unit pole is one which is totally inadequate for the discussion of the correspondence of the magnetic fields as measured in the two systems S and S'. It could only attain precision by the incorporation of ideas concerned with the equation of motion of a unit pole, in a manner analogous to that adopted in considering the equation of motion of an electron. The spirit of the idea concerned with the hypothetical action of a magnetic field on a unit pole is contained in the physical fact of the action of a magnetic field on a moving electron. One has only to recall that the couple on an elementary magnet is, in the sense of its physical realization, a representative of the force due to the

magnetic field on a revolving electron. If therefore one wishes to define a magnetic field in terms of the force on some assigned entity, the moving electron is the logical thing to choose, and it is in the spirit of this idea that we shall now proceed to our definition.

Let us suppose that there exists a vector $\mathbf{P}$ which is a function of the motion of an electron, such that $k\mathbf{P}$, $ki(\mathbf{Pw})/c$ is a 4-vector, and such that

$$\mathbf{E} + \frac{[\mathbf{wH}]}{c} = \mathbf{P} \tag{44}$$

where $\mathbf{E}$ is defined as the value of $\mathbf{P}$ when $\mathbf{w}=0$ and $\mathbf{H}$ is defined as the limit of $c(|\mathbf{P}-\mathbf{E}|)/w$ when w is zero, the understanding being that $|\mathbf{P}-\mathbf{E}|$ represents the scalar value of the difference of the vectors, and w is the scalar value of the velocity, and where it is further understood that, in proceeding to the limit, the direction of the vector is always chosen so as to make $(|\mathbf{P}-\mathbf{E}|)/w$ a maximum. The direction of $\mathbf{H}$ is defined in the sense implied by the direction of the vector product $[\mathbf{wH}]$ as determined by its equality with $c(\mathbf{P}-\mathbf{E})$ for the limiting (zero) value of $\mathbf{w}$. These definitions are consistent with the limiting cases of (44). They of course do not necessarily imply (44) for cases other than the limiting cases. If, however, we assume that (44) holds for all values of the velocity, we may conclude as follows: In the first place, (44) implies, immediately,

$$(\mathbf{E} \cdot \mathbf{w}) = (\mathbf{P} \cdot \mathbf{w}) \tag{45}$$

Since it is an *algebraical* fact that, with $\mathbf{E}'$ and $\mathbf{H}'$ defined by (25) and (26), the quantities

$$k'\left(\mathbf{E}' + \frac{[\mathbf{w}'\mathbf{H}']}{c}\right), \qquad k'i(\mathbf{E}' \cdot \mathbf{w}')/c$$

are related to

$$k\left(\mathbf{E} + \frac{[\mathbf{wH}]}{c}\right), \qquad ki(\mathbf{E} \cdot \mathbf{w})/c$$

by the transformation of a 4-vector, and since $k\mathbf{P}$, $ki(\mathbf{P} \cdot \mathbf{w})/c$ is a 4-vector, we have

$$\mathbf{E}' + \frac{[\mathbf{w}'\mathbf{H}']}{c} = \mathbf{P}' \tag{46}$$

By considering the limiting case where $\mathbf{w}'=0$, however, we find

$$\mathbf{E}' = \mathbf{P}'_{\mathbf{w}'=0}$$

But by the definition of $\mathbf{E}_0'$ which corresponds in S' to the definition taken for $\mathbf{E}$ in S, we have

$$\mathbf{E}_0' = \mathbf{P}'_{w'=0}$$

Hence $\mathbf{E}' = \mathbf{E}_0'$.

Similarly, by proceeding to a limit with (46) in the manner adopted for the definition of $\mathbf{H}$, we conclude that $\mathbf{H}' = \mathbf{H}_0'$.

We shall define ρ as div $\mathbf{E}$ and σ as div $\mathbf{H}$, and shall postulate[6] that the densities ρ_0' and σ_0' in the system S' are related to the densities ρ and σ in S in such a way that for corresponding elements of volume $d\tau$ and $d\tau'$,

$$\rho_0' d\tau' = \rho d\tau\,; \qquad \sigma_0' d\tau' = \sigma d\tau$$

which lead, as is well known to

$$\rho_0' = \beta\rho\left(1 - \frac{u_x v}{c^2}\right)\,; \qquad \sigma_0' = \beta\sigma\left(1 - \frac{v_x v}{c^2}\right)$$

Since $\mathbf{E}'$ and $\mathbf{H}'$ have been shown to be the appropriate fields for the system S', the criterion of invariance requires

$$\text{div}'\,\mathbf{E}' = \rho_0' = \beta\rho\left(1 - \frac{u_x v}{c^2}\right) \tag{47}$$

and

$$\text{div}'\,\mathbf{H}' = \sigma_0' = \beta\sigma\left(1 - \frac{v_x v}{c^2}\right) \tag{48}$$

Using (25) and (47)

$$\frac{\partial E_x}{\partial x'} + \frac{\partial}{\partial y'}\beta\left(E_y - \frac{v}{c}H_z\right) + \frac{\partial}{\partial z'}\beta\left(E_z + \frac{v}{c}H_y\right) = \beta\rho\left(1 - \frac{u_x v}{c^2}\right)$$

so that, in view of (20)

$$\beta\,\text{div}\,\mathbf{E} + \frac{\beta v}{c^2}\frac{\partial E_x}{\partial t} + \frac{\beta v}{c}\left(\frac{\partial H_y}{\partial z} - \frac{\partial H_z}{\partial y}\right) = \beta\rho\left(1 - \frac{u_x v}{c^2}\right)$$

so that, since $\rho = \text{div}\,\mathbf{E}$

$$\frac{1}{c}\left(\rho u_x + \frac{\partial E_x}{\partial t}\right) = \frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z}$$

We need only rely upon symmetry with regard to all directions in space to conclude

$$\frac{1}{c}\left(\rho\mathbf{u} + \frac{\partial \mathbf{E}}{\partial t}\right) = \text{curl}\,\mathbf{H}$$

[6] The postulate implies the invariance of electric and magnetic charge.

In an exactly similar manner, using (26) and (48) we find

$$-\frac{1}{c}\left(\sigma \mathbf{v} + \frac{\partial \mathbf{H}}{\partial t}\right) = \text{curl } \mathbf{E}$$

so that since we also have $\rho = \text{div } \mathbf{E}$ and $\sigma = \text{div } \mathbf{H}$ the equations (1)–(4) are established in the generalized form with the σ terms. The omission of the σ terms is the equivalent of restricting our interests to those problems where σ is zero. These we believe to comprise all natural phenomena.

SLOANE LABORATORY,
YALE UNIVERSITY,
June 1, 1926.

THE THEORY OF WIMSHURST'S ALTERNATING STATIC MACHINE

By A. W. Simon[1]

Abstract

The quantitative theory of Wimshurst's alternating static machine is developed in detail according to the general method previously given by the author for other static machines. The theory predicts that the potential of any element of the machine will reverse at definite intervals and at the same time increase in value. While the exact period of reversal depends on the capacities involved in the machine, the approximate period can be calculated and is found to be the time of one revolution rather than the time of three quarters of a revolution as observed by Wimshurst. An actual machine was constructed and the reversal observed by means of the glow in discharge tubes. It was found that such a machine does reverse every revolution rather than every three quarters of a revolution. The theory given can be extended to other machines of the same type with more than four inductors. The period of reversal of a six-inductor machine is calculated to be approximately the same as that of a four-inductor machine.

SOME thirty years ago Wimshurst[2] described an experimental influence machine which had the peculiar property of reversing its polarity with the greatest regularity,—a reversal occurring, according to Wimshurst, every three quarters of a revolution. The present wo k is concerned with the explanation of the action of a machine of this type.

The machine studied in detail is represented diagrammatically in Fig. 1, from which its essential elements and mode of operation can be seen readily. If we number the elements as indicated in the figure, set up the equations for the charges for two successive quarter turns, and then eliminate the charges by substituting for each charge its value in terms of the electric coefficients and the corresponding potentials, according to the general method outlined in previous papers,[3] we have eight equations, the left members of which involve as unknowns linearly the eight potentials, $V_0(n+1)$, $V_1(n+1)$, $\cdots$ $V_7(n+1)$; and the right members of which involve as unknowns linearly the eight potentials $V_0(n)$, $V_1(n)$, $\cdots$ $V_7(n)$; and in which the matrix of the coefficients on either side is a square matrix of the eighth order, involving as elements certain sums of the electric coefficients.

[1] National Research Fellow.

[2] J. Wimshurst, Phil. Mag. **31**, 507 (1891).

[3] A. W. Simon, Phys. Rev. **24**, 690 (1924; also Phil. Mag. **49**, 257 (1925).

The two matrices in question can be represented very conveniently by means of the scheme already given in a previous paper;[4] in particular, the matrix of the coefficients of the *left* members is obtained by writing at the heads of the *columns* and also at the heads of the *rows* of an eighth order matrix the numbers: 0,8; 1,9;2,10; 3,11; 4; 5; 6; 7; while the matrix of the coefficients of the *right* members is given by writing at the heads of the *columns* of an eighth order matrix the numbers just given and at the heads of the rows the numbers 0,6; 1,7; 2,4; 3,5; 8,9; 10; 11. Any cell of these matrices then represents the coefficient occupying the corresponding place in the matrix of the coefficients of the fundamental

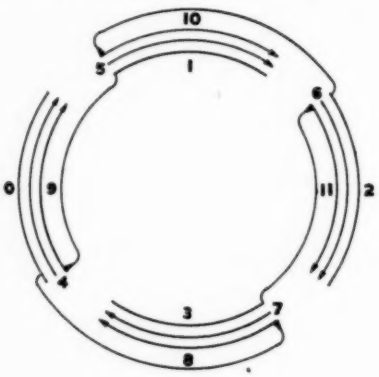


Fig. 1. Diagrammatic representation of Wimshurst's alternating static machine

potential equations, and this coefficient is obtained in terms of the coefficients of capacity and coefficients of induction of the elements of the machine by combining the numbers at the head of the column in which the coefficient stands with the numbers at the head of the row according to the notation[5]:

$$a_{p,q\,.\,r,s} \equiv a_{p,r} + a_{p,s} + a_{q,r} + a_{q,s} ,$$

where $a_{i,i}$ represents the coefficient of capacity of the conductor indexed i, and $a_{i,j}$ represents the coefficient of induction of the conductors indexed i and j.

Due to the fourfold geometrical symmetry of the machine the two matrices are, furthermore, respectively of the form

$$\begin{vmatrix} M_1 & M_2 \\ M_3 & M_4 \end{vmatrix} , \quad \begin{vmatrix} M_5 & M_6 \\ M_7 & M_8 \end{vmatrix} , \tag{1}$$

[4] A. W. Simon, Phys. Rev. **28**, 142 (1926).

[5] This modification of our previous notation is necessitated by the fact that in the present case some of the subscripts are numbers of two digits.

where each of the symbols M_i represents a cyclic matrix of the fourth order, i.e., M_i is of the form:

$$\begin{vmatrix} a_i & d_i & c_i & b_i \\ b_i & a_i & d_i & c_i \\ c_i & b_i & a_i & d_i \\ d_i & c_i & b_i & a_i \end{vmatrix} \tag{2}$$

The quantities a_i, b_i, c_i, d_i, in turn are given, for $i=1, 2, \cdots 8$, in terms of the coefficients of capacity and coefficients of induction of the elements of the machine in the configuration of Fig. 1, if we again make use of the representation defined in a previous work, by:

	0,8	1,9	2,10	3,11	4	5	6	7
0,8	a_1	d_1	c_1	b_1	a_2	d_2	c_2	b_2
4	a_3	d_3	c_3	b_3	a_4	d_4	c_4	b_4
0,6	a_5	d_5	c_5	b_5	a_6	d_6	c_6	b_6
8	a_7	d_7	c_7	b_7	a_8	d_8	c_8	b_8

(3)

I. Mathematical Solution

The method of solution of a system of equations of this type has already been pointed out in a previous paper.[6] If we employ the method there described, we derive a set of auxiliary equations of the form:

$$\begin{aligned} A_{1j}Z_{1j}(n+1)+A_{2j}Z_{2j}(n+1) &= A_{5j}Z_{1j}(n)+A_{6j}Z_{2j}(n) , \\ A_{3j}Z_{1j}(n+1)+A_{4j}Z_{2j}(n+1) &= A_{7j}Z_{1j}(n)+A_{8j}Z_{2j}(n) , \end{aligned} \tag{4}$$

where the Z's are defined by:

$$\begin{aligned} Z_{1j}(n) &\equiv [V_0(n)w_j^0+V_1(n)w_j^1+V_2(n)w_j^2+V_3(n)w_j^3] , \\ Z_{2j}(n) &\equiv [V_4(n)w_j^0+V_5(n)w_j^1+V_6(n)w_j^2+V_7(n)w_j^3] , \end{aligned} \tag{5}$$

and the quantities A_{ij} are defined by:

$$A_{ij} \equiv [a_i w_j^0+b_i w_j^1+c_i w_j^2+d_i w_j^3] . \tag{6}$$

As the solutions of (4) we have at once[7] a set of equations of the form:

$$\begin{aligned} Z_{1j}(n) &= C_{1j}r_{1j}^n+C_{2j}r_{2j}^n \\ Z_{2j}(n) &= C_{1j}'r_{1j}^n+C_{2j}'r_{2j}^n \end{aligned} \tag{7}$$

where r_{1j} and r_{2j} are the roots of the algebraic equation:

$$f_j(r) \equiv \begin{vmatrix} A_{1j}r-A_{5j} & A_{2j}r-A_{6j} \\ A_{3j}r-A_{7j} & A_{4j}r-A_{8j} \end{vmatrix} = 0 \tag{8}$$

[6] A. W. Simon, Phys. Rev. **27** 747 (1926).

[7] G. Boole, "A Treatise on the Calculus of Finite Differences," Chap. XI

and the C's are certain arbitrary constants to be determined.

From (7) we can deduce at once the formulas for the quantities $V_s(n)$; we have merely to note that from the definition of the Z's namely (5), it follows:

$$\begin{aligned} 4V_s(n) &= \sum_{j=0}^{3} Z_{1j}(n)/w_{sj}\,, \qquad s=0,\ 1,\ 2,\ 3, \\ 4V_s(n) &= \sum_{j=0}^{3} Z_{2j}(n)/w_{sj}\,, \qquad s=4,\ 5,\ 6,\ 7\,; \end{aligned} \tag{9}$$

whence, taking account of (7), we have finally:

$$\begin{aligned} 4V_s(n) &= \sum_{j=0}^{3} [C_{1j}r_{1j}{}^n+C_{2j}r_{2j}{}^n]/w_{sj}\,, \qquad s=0,\ 1,\ 2,\ 3\,; \\ 4V_s(n) &= \sum_{j=0}^{3} [C_{1j}{}'r_{1j}{}^n+C_{2j}{}'r_{2j}{}^n]/w_{sj}\,, \qquad s=4,\ 5,\ 6,\ 7\,. \end{aligned} \tag{10}$$

The problem therefore reduces to the study of the right members of (7), in particular, to the study of the arbitrary constants.

II. Evaluation of the Arbitrary Constants

If now we put $n=0$ in (4), substitute for the Z's the values given by (7), and solve for C_{1j}' and C_{2j}' in terms of C_{1j} and C_{2j}, we have, since $f_j(r_{1j})=f_j(r_{2j})=0$:

$$C_{1j}'=\underline{\overline{K}}_{1j}C_{1j}\,, \qquad C_{2j}'=\underline{\overline{K}}_{2j}C_{2j}\,; \tag{11}$$

where the K's are certain constants given by:

$$\begin{aligned} \underline{\overline{K}}_{1j}D &= \begin{vmatrix} A_{1j}r_{1j}-A_{5j} & A_{2j}r_{2j}-A_{6j} \\ A_{3j}r_{1j}-A_{7j} & A_{4j}r_{2j}-A_{8j} \end{vmatrix}\,, \\ \underline{\overline{K}}_{2j}D &= \begin{vmatrix} A_{2j}r_{1j}-A_{6j} & A_{1j}r_{2j}-A_{5j} \\ A_{4j}r_{1j}-A_{8j} & A_{3j}r_{2j}-A_{7j} \end{vmatrix}\,, \\ D &\equiv (r_{1j}-r_{2j}) \begin{vmatrix} A_{2j} & A_{6j} \\ A_{4j} & A_{8j} \end{vmatrix}\,. \end{aligned} \tag{12}$$

If next we put $n=0$ in (7), substitute for C_{1j}' and C_{2j}' the values just found, and solve for C_{1j} and C_{2j}, we have:

$$\begin{aligned} C_{1j} &= [\underline{\overline{K}}_{2j}Z_{1j}(0)-Z_{2j}(0)]/[\underline{\overline{K}}_{2j}-\underline{\overline{K}}_{1j}]\,, \\ C_{2j} &= [Z_{2j}(0)-\underline{\overline{K}}_{1j}Z_{1j}(0)]/[\underline{\overline{K}}_{2j}-\underline{\overline{K}}_{1j}]\,. \end{aligned} \tag{13}$$

The relations (11) and (13) exhibit three important results: (1) If $C_{1j}=0$, then also $C_{1j}'=0$; if $C_{2j}=0$, then also $C_{2j}'=0$. (2) If $Z_{2j}(0)=\underline{\overline{K}}_{1j}Z_{1j}(0)$, then $C_{2j}=0$ and $C_{1j}=Z_{1j}(0)$; if $Z_{2j}(0)=\underline{\overline{K}}_{2j}Z_{1j}(0)$, then

$C_{1j}=0$ and $C_{2j}=Z_{1j}(0)$. (3) Finally, if $Z_{1j}(0)=Z_{2j}(0)=0$, then also $C_{1j}=C_{1j}'=C_{2j}=C_{2j}'=0$.

III. Particular Solutions of the Voltage Equations

The results just given show that for certain relations between the quantities $V_s(0)$, the general solution reduces to simple forms. In particular, if the original potentials satisfy the relations:

$$\begin{aligned} &V_s(0)=E(0)\cos(s-p)k2\pi/4, && s=0,\ 1,\ 2,\ 3\ ; \\ &V_s(0)=\kappa_{ij}E(0)\cos[(s-p)k2\pi/4+\Psi_{ij}]\ , && s=4,\ 5,\ 6,\ 7\ ; \end{aligned} \tag{14}$$

where s, p, and $-k$ take the values 0, 1, 2, 3, and κ_{ij} and ψ_{ij} are defined by:

$$\underline{\overline{K}}_{ij}\equiv\kappa_{ij}(\cos\Psi_{ij}+i\sin\Psi_{ij})\ , \tag{15}$$

the general solution reduces to:

$$\begin{aligned} &V_s(n)=\rho_{ij}{}^nE(0)\cos[n\theta_{ij}+(s-p)k2\pi/4]\ , && s=0,\ 1,\ 2,\ 3\ ; \\ &V_s(n)=\rho_{ij}{}^n\kappa_{ij}E(0)\cos[n\theta_{ij}+(s-p)k2\pi/4+\Psi_{ij}]\ , && s=4,\ 5,\ 6,\ 7\ ; \end{aligned} \tag{16}$$

where r_{ij} has been written in the form:

$$r_{ij}\equiv\rho_{ij}(\cos\theta_{ij}+i\sin\theta_{ij})\ . \tag{17}$$

IV. Computation of the Roots and Constants

For the interpretation of the results we require the numerical values of the quantities r_{ij} and $\underline{\overline{K}}_{ij}$. These are functions, by virtue of (8), (12), (6) and (3), only of the coefficients of capacity and coefficients of induction of the twelve elements of the machine in a certain position, namely that in which the carriers just break contact with the brushes (Fig. 1). These coefficients, of course, it is impossible to calculate, so that it would be necessary in order to complete the analysis of any given machine to actually measure them.

However, we can determine the approximate values of the quantities r_{ij} and $\underline{\overline{K}}_{i,j}$ if we put $a_{0,0}=a$, $a_{9,9}=ca$, $a_{4,4}=(c+1)a$, $a_{0,4}=(e-a)$, $a_{9,4}=c(e-a)$, and all the other coefficients $a_{i,j}$ equal to 0. These conditions, it may be noted, will be approximately satisfied if the inductors and carriers are identical in shape and dimensions, and if the distance between the members of each group of adjacent elements (0,4,9, for example) is small compared to their distance away from the elements of the other groups.

Substituting the values just given in (8) and (12), solving for r_{ij} and $\underline{\overline{K}}_{ij}$ in terms of c, a, e, and finally taking the limit as $e\to 0$ (the latter procedure is necessary to avoid indeterminate forms in the case of $f_0(r)$

and $f_2(r)$), we have the following set of values for the quantities r_{ij} and $\underline{\overline{K}}_{ij}$:

j	r_{1j}	r_{2j}	$\underline{\overline{K}}_{1j}$	$\underline{\overline{K}}_{2j}$
0	1	$-1/(1+c)$	1	-1
1	$1+i$	$-i$	$\dfrac{2c(c+2)-i(4c+5)}{2c(c+3)+5}$	1
2	1	0	1	-1
3	$1-i$	$+i$	$\dfrac{2c(c+2)+i(4c+5)}{2c(c+3)+5}$	1

In addition it is important to note that two of the r's are identically equal to unity irrespective of what the capacities involved in the machine are. In order to prove this it is convenient to introduce a new symbol s_{ij}, which is defined as the sum of all those coefficients which have as subscripts the combinations which result from the pairing off of i with the numbers of those elements of the machine which are similarly placed with respect to the element indexed j. As groups of similarly placed elements we have those indexed 0,1,2,3; 4,5,6,7; and 8,9,10,11. In terms of this notation $f_0(r)$ becomes:

$$f_0(r) = \begin{vmatrix} r(s_{00}+s_{09}+s_{90}+s_{99})-(s_{00}+s_{04}+s_{90}+s_{94}), & r(s_{40}+s_{49})-(s_{44}+s_{40}) \\ r(s_{04}+s_{94}) \qquad -(s_{09}+s_{99}) \qquad , & r(s_{44}) \qquad -(s_{49}) \end{vmatrix}$$

from which it is obvious that $f_0(r)$ vanishes for $r=1$.

The notation s_{ij} is very convenient when large numbers of elements must be dealt with; in fact the proof just given applies at once to any alternator of this type irrespective of the number of inductors.

A similar proof can be given for $f_2(r)$ provided we introduce the notation d_{ij} which we define to be similar to s_{ij} except that the signs of the successive terms of the sum are alternately $+$ and $-$. In particular for example: $d_{0,4} \equiv +a_{0,4}-a_{0,5}+a_{0,6}-a_{0,7}$.

V. Physical Interpretation of the Results

From (10) and the table of values of the r's, we note at once that for large values of n, (theoretically only after an infinite number of quarter turns but practically after a few revolutions) the potentials are given by:

$$\begin{aligned} V_s(n) &= C_{11}r_{11}{}^n/w_{s1}+C_{13}r_{13}{}^n/w_{s3}\,, \qquad s=0,\ 1,\ 2,\ 3\,; \\ V_s(n) &= \underline{\overline{K}}_{11}C_{11}r_{11}{}^n/w_{s1}+\underline{\overline{K}}_{13}C_{13}r_{13}/w_{s3}\,, \qquad s=4,\ 5,\ 6,\ 7\,. \end{aligned} \tag{18}$$

If next we write each quantity appearing in (18) in trigonometric form and note that the two terms on the right-hand side are conjugate complex quantities, these equations become:

$$V_s(n)=R_{11}\rho_{11}^n[\cos n\,\theta_{11}+\Delta_{11}-s\pi/2]\,, \qquad s=0,\ 1,\ 2,\ 3\,;$$
$$V_s(n)=\kappa_{11}R_{11}\rho_{11}^n[\cos n\,\theta_{11}+\Delta_{11}-s\pi/2+\Psi_{11}]\,, \quad s=4,\ 5,\ 6,\ 7\,; \tag{19}$$

where, if we write C_{11} in the form $C_{11}\equiv A_{11}+iB_{11}$, R_{11} and Δ_{11} are defined by: $R_{11}\equiv\sqrt{A_{11}^2+B_{11}^2}$ and $\Delta_{11}\equiv\arctan B_{11}/A_{11}$.

From these equations it is seen that *the potential of any element will alternate and at the same time increase in value*—a result which is in accordance with the observation of Wimshurst that such a "machine is self-exciting notwithstanding that when at work its electrical charges alternate."

Moreover, we can add that eventually the potentials of the inductors ($s=0,1,2,3$) taken in the direction of rotation will be $\pi/2$ out of phase; that the same will be true of the potentials of the insulated carriers ($s=4,5,6,7$); while the potential of any insulated carrier will be proportional to the potential of the adjacent inductor but will differ in phase from it by an angle ψ.

Let us next inquire what the theoretical frequency of alternation will be. This will depend, for any particular machine, on the numerical values of the electric coefficients, and for the reasons given above can be calculated only approximately. However, if we use the approximate values for r_{11} given in the table above, we have $\theta_{11}=\pi/4$, whence it follows that *the potential of any element should reverse approximately every revolution*, rather than every three quarters of a revolution as was observed by Wimshurst.

It is also to be noted that ρ_{11} comes out approximately equal to $\sqrt{2}$ from which it follows that the potential of any element should be approximately quadrupled every revolution—a result which is interesting because it is the same as that obtained for the case of a four-inductor alternator of the type described by the writer.[8]

To the results just given we can add a number of others which we deduce from the particular solutions. Of these three are of interest:

(1) $V_s(0)=E_0(0)$, for $s=0,1,2,3$; $V_s(0)=E_4(0)$, for $s=4,5,6,7$; and, further, $E_4(0)=\underline{K}_{10}E_0(0)$. The corresponding solution is, since $r_{10}=1$, for every n from 0 to ∞: $V_s(n)=E_0(0)$, for $s=0,1,2,3$; $V_s(n)=E_4(0)$, for $s=4,5,6,7$; that is to say, no change takes place.

(2) $V_s(0)=E_0(0)\cos(s-p)(-\pi)$, for $s=0,1,2,3$; $V_s(0)=E_4(0)$ co-$(s-p)(-\pi)$, for $s=4,5,6,7$; and further $E_4(0)=\underline{K}_{12}E_0(0)$. The cors responding solution is, since $r_{12}\equiv 1$, for every n from 0 to ∞: $V_s(n)=E_0(0)\cos(p-s)\pi$, for $s=0,1,2,3$: $V_s(n)=E_4(0)\cos(p-s)\pi$, for $s=4,5,6,7$; that is to say, for this case also, no change takes place.

[8] A. W. Simon, Phys. Rev. **25**, 368 (1925).

(3) $V_s(0)=E(0)\cos[(s-p)(-\pi/2)]$, for $s=0,1,2,3$; $V_s(0)=\kappa_{11}E(0)\cos[(s-p)(-\pi/2)+\psi_{11}]$, for $s=4,5,6,7$; for this case we have, for every n from 0 to ∞:

$$\begin{aligned} V_s(n)&=\rho_{11}{}^n E(0)\cos[n\theta_{11}+(p-s)\pi/2]\,, \qquad s=0,\ 1,\ 2,\ 3\,; \\ V_s(n)&=\rho_{11}{}^n\kappa_{11}E(0)\cos[n\theta_{11}+(p-s)\pi/2+\Psi_{11}]\,, \quad s=4,\ 5,\ 6,\ 7\,. \end{aligned} \tag{20}$$

Comparing (19) and (20) we note that the potentials of the various elements of the machine tend toward the state in which the potentials satisfy (19); that this state is attained when the transient terms (those corresponding to $|r|\leqq 1$) have become negligible; and, finally, that if the system is originally in this state, then the transient terms are absent altogether.

VI. Experimental Test of the Theory

The discrepancy between our theoretical result, that the potential of any element should reverse approximately every revolution, and the experimental result of Wimshurst that it reverses every three quarters of a revolution, obviously requires further investigation. Toward this end an actual machine satisfying the conditions we have laid down in the previous discussion was constructed. In particular, it consisted of two fixed glass discs 30″ in diameter and a rotating glass disc 27″ in diameter, each of the fixed discs carrying two inductors placed with their centers 180° apart, and the rotating disc carrying eight sectors, four on each side, placed exactly opposite one another, with their centers 90° apart. The inductors and carriers were all of the same size and shape, being sections of a ring of tinfoil with an inner diameter of $6\frac{3}{4}$″ and an outer diameter of $12\frac{1}{2}$″, each section subtending an angle of 45° at the center.

The rotating disc was placed between the two fixed discs, and the latter were mounted so that the center lines of the successive inductors were 90° apart, but so that alternate inductors were on opposite sides of the rotating disc. The inductors were also on the outside faces of the fixed discs, so that a thickness of glass intervened between each inductor and the nearest carrier. The inductors and carriers were so mounted that as each pair of carriers came directly in front of an inductor, the three elements of the group exactly covered one another.

Brushes were so placed as to connect the outside carrier of each pair of rotating carriers to the inductor next following in the direction of rotation, and were adjusted to break contact at the instant when the carriers left the position directly in front of the inductors (Fig. 1). The glass discs were shellac varnished, and the brush holders insulated with hard rubber.

The reversal was observed first by means of small paper electroscopes according to the method of Wimshurst, but these were not found to work very consistently.

An improved method was to insert into one or more of the brush circuits, i.e., between brush and inductor, a straight gaseous discharge tube and observe the glow in this tube. In this way the period of reversal could be very accurately observed, and it was found that *the reversal actually did occur every revolution* rather than every three quarters of a revolution, as stated by Wimshurst.

VII. Extension of the Theory

As already pointed out in a previous paper[6] machines of the type just discussed can be constructed with more than four inductors, in particular with 6 inductors and 12 carriers, or, in general, with $2m$ inductors and $4m$ carriers, and the theory just given can be extended immediately to these machines. We have merely to let j take the values $0, 1, \ldots . 2m$, in the equations given above.

It is of interest to inquire what the frequency of alternation of a six-inductor machine would be. If the theory of such a machine (6 inductors, 12 carriers) is developed it is found that for this case also the theoretical frequency is approximately one alternation per revolution, and this is very likely true for every machine of this type, that is to say: increasing the number of inductors does not greatly change the frequency of alternation.

The theory given can also be extended to the case of a machine with 4 inductors and 16 carriers; or, in general, to the case of 2m inductors and 8m carriers. The previous case reduced, as we saw from Eq. (8), to the solution of quadratic equations, the present case would reduce to the solution of biquadratic equations.

For machines with a larger number of carriers than $8m$, the solution of algebraic equations of degree greater than the fourth would be required, so that algebraic methods would probably fail. Whether it is possible to solve these more complicated types has not been investigated; it would be desirable, however, to investigate these cases with a view to solving the case of a very large number (theoretically an infinite number) of carriers, since this would approximate a *sectorless*, i.e., a plain glass disc, machine. In fact, the theory developed by the author applies only to *sectored* machines; the theory of *sectorless* machines still remains to be developed.

Norman Bridge Laboratory,
California Institute of Technology
Pasadena, California.
June 18, 1926.

A TEST OF THE EXISTENCE OF THE CONDUCTING LAYER

By G. Breit and M. A. Tuve

Abstract

A method previously proposed for a test of the existence of ionization in the upper atmosphere has been developed, and a definite proof of the *existence of echoes from the upper regions* has been obtained. The echoes are present for 70-meter waves with an 8-mile base near Washington, D. C. The effective height of the layer is between 50 and 130 miles. At times multiple reflections are present. *Radio fading* is shown to be not only an effect of interference between the ground and the reflected waves, but also to a large extent an effect of the presence or absence of reflected waves. A *seasonal variation* in the effective height between summer and fall seems to exist. A smaller *diurnal effect* is also suspected. The height seems greater in the fall than in the summer and greater in the afternoon than in the morning. *Effects of wave-length and of location* have been studied. A quantitative discussion of the results enables one to eliminate too gradual distributions of electron density. The measured retardation is shown to correspond to a height greater than the actual by amounts differing for various polarizations of the refracted waves.

WITH the development of the sciences of radio and of terrestrial magnetism it has become probable that the upper atmosphere is ionized sufficiently to reflect electromagnetic waves. However, the evidence obtained has not been quite direct until recently, when Appleton and Barnett have completed their work. For this reason we have undertaken an oscillographic study of radio signals with the purpose of observing the echo from the layer. We have described the method previously,[1] but for purposes of completeness it is here described again. A transmitting station is operated so as to send out what is commonly called I.C.W.; it is a set of interrupted trains of waves. The duration of each train is made to be about 1/1000 second. At the receiving end the signal is detected, amplified, and oscillographed. The oscillogram may either show a single set of humps corresponding to a single path transmission, or else it may show two or more sets of humps corresponding to the existence of echoes. From the displacement of the echo with respect to its origin, the retardation between the reflected and the directly received wave is ascertained.

Experimental Arrangements

(a) *Transmission from Bellevue.* Arrangements for transmission have been made with the Naval Research Laboratory (station *NKF*, Bellevue,

[1] M. A. Tuve and G. Breit, Terr. Mag. **30**, 15–16 (1925); G. Breit and M. A. Tuve, Nature **116**, 357 (1925).

Anacostia, D.C.), the Westinghouse Electric and Manufacturing Company (station *KDKA*, Pittsburgh, Pa.), the Radio Corporation of America (station *WSC*, Tuckerton, N. J.), the Bureau of Standards (station *WWV*, Washington, D. C.), and several of the enthusiastic amateurs residing in Washington. The most definite results have been obtained from the Naval Research Laboratory owing to the fortunate relative location of the two laboratories and to the high constancy of the frequency emitted by the *NKF* transmitter. This is achieved by the use of crystal control and makes it superior to any of the other stations we tried for the purpose in question. The interruptions in the wave trains were obtained by supplying the amplifier tubes of the transmitter with alternating current while the master oscillator was fed on direct current. This gave a constant frequency and the required type of modulation. The frequency of alternating current used was 500, and the "on" time of the wave trains has been varied to some extent (1/3 to 1/5) of a cycle) by changing the biasing grid voltages. These arrangements have been kindly made for us by Dr. A. H. Taylor and his assistants, Messrs. L. A. Gebhardt and L. C. Young. After the first definite indications of the reflections have been obtained on 70 meters, the wave form of the transmitter was investigated by means of an oscillograph quite similar to the one used in the reception experiments. A single detector tube was first of all coupled to the antenna of the transmitter by means of a coil with connecting leads shielded in a lead tube, the shield being grounded. The output of the detector was applied to the input of a power amplifier containing four tubes of type 202 (5 watts each) used in parallel. The connections of the amplifier will be described in detail in connection with the receiving apparatus. The output of the amplifier was fed through the oscillograph. Visual observations made by means of a rotating mirror showed that the wave form consisted of a single set of humps. The observations taken by coupling directly to the antenna were not very reliable because they had to be taken directly in the gallery containing the 5 k.w. transmitter, and consequently had to be carried through in a hurry under unfavorable conditions of vibration. The apparatus was consequently transferred into another building of the Naval Research Laboratory, and there the signals were received by means of a small antenna as well as a loop on the single-tube detector as before. The wave form appeared to correspond closely to a single set of humps. However, a slight presence of radiation in the "off" time was detected. The effect could not be due to a reflection, the directly received wave being too strong in comparison. The difficulty was eliminated by

using a little additional grid bias in the transmitter. The exact cause of this radiation in the "off" time is unknown, though according to Dr. A. H. Taylor it may be due to certain transient effects in the transmitter circuit. Since care was taken to eliminate the transient effect in all of the transmitters operated by Bellevue, it is safe to assume that the wave form sent out was accurately single-humped with the exception of the first two tests. However, even in these the transient effect was about 1/10 of the reflections observed.

(b) *Receiving and oscillographic equipment.* The signals were received in most cases by means of an open antenna connected to ground through the primary of a loose coupler, the secondary of which was connected to the input terminals of a superheterodyne set. The connections were as shown in Fig. 1. Here the tubes are represented in the usual manner. The first tube (1) is the first detector. Its input terminals I_1, I_2 are connected to the secondary of the loose coupler or else to a loop (coil aerial)

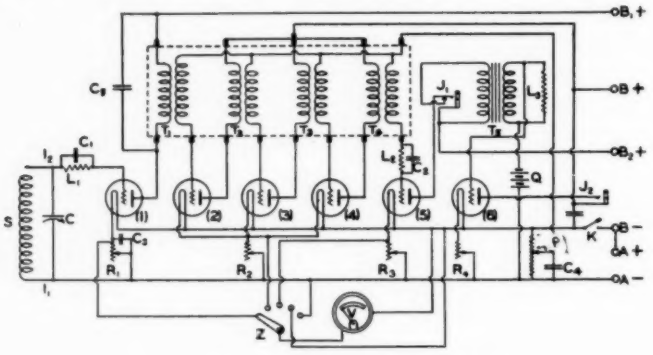


Fig. 1. Wiring diagram of superheterodyne set.

shown as S. S is also coupled to an oscillator giving an adjustable frequency differing from the frequency of the received wave by about 50 K.C. The detection takes place by means of the grid-leak condenser L_1C_1, with $L_1=2$ m.Ω, $C_1=.00025$ microfarad. The tube (1) was entirely enclosed in a brass box. This eliminated to some extent complications arising from the presence of the original frequency in the other tubes. The output of (1) passes through the primary of the transformer T_1 which as well as T_2, T_3, T_4 is tuned to 50 K.C. The condenser C_5 serves to filter out the high frequency from the remaining tubes. Condenser C_3 served the same purpose and had the value .005 microfarad. Tubes (2), (3), (4) amplify the intermediate frequency 50 K.C. which is then detected in (5) by means of leak condenser L_2C_2, with $L_2=1$ m.Ω, $C_2=.00025$ microfarad. The plate voltage for (1) is supplied through

B_1+, to (2), (3), (4), (6) through B+, and to (5) through B_2+. The output of the set was connected to the power amplifier by means of the jack J_1 which, when plugged, disconnected (6) from the circuit. The transformer T_5 is an audio-frequency transformer, and the stray coupling to it was sufficient to hear the signals if the power amplifier was connected through J_1 and phones were connected to J_2. The battery Q kept the grid of (6) at the proper potential. It had a value of 6 volts. The potentiometer P by-passed by condenser C_4 (=.006 microfarad) controlled the regeneration in (2), (3), (4). The voltmeter V could be connected to either of the tubes or to the battery by means of a voltmeter switch with contact arm Z. The transformers T_1, T_2, T_3, T_4 were bought in one unit called the Precise Multiformer and manufactured by the Precise Manufacturing Corporation, Rochester, New York. The description of the auxiliary oscillator is unnecessary in this connection. The tubes used were type 201*A* of the Radio Corporation.

The connections of the power amplifier were as shown in Fig. 2. The output of tube (5) is passed through a resistance of 25,000 ohms. The

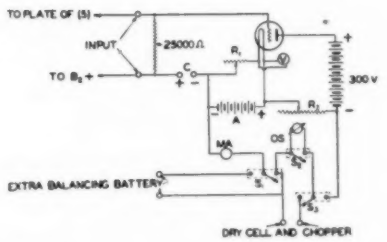


Fig. 2. Wiring diagram of power amplifier.

fluctuations of the potential across this resistance are applied to the grid of the amplifier. The oscillograph element *Os* is protected by the short circuiting switch S_2. With switches S_1, S_3 closed to the right on the figure, the plate current through the milliammeter *MA* is balanced out by a connection from the *A* battery through R_2. R_2 had a range of 0–800 ohms (two 400-ohm potentiometers). By means of S_1 an extra balancing voltage could be applied to *Os*, and by means of S_3 tests for distortion in the oscillograph element itself could be made by connecting it to a chopper and dry cell and thus passing through it a rectangular current wave.

In the power amplifier of Fig. 2, four or five tubes of 5 watts each (type 202 of Radio Corporation) were used in parallel. The 300-volt plate potential was applied by means of storage batteries for the photographs

here published. However, satisfactory results could be also obtained by means of dry cells.

Various tests of the performance of the apparatus were carried through and tests for distortion were made with the following results.

The oscillograph element used was of the usual oil-immersed General Electric type. It was supplied with the standard and the high-sensitivity elements and with the usual silver-strip type of suspension. It was found that, while the silver-strip suspension was fairly satisfactory, tungsten wire was more so. The use of this was kindly suggested to us by Dr. Eckhardt, formerly of the Bureau of Standards. Best results for the purpose of oscillographing at high frequency were obtained with the SV element remodeled by soldering the tungsten wire to a heavy copper wire somewhat above the higher bridge. This eliminates the vibrational effect due to the rigidity of the W wire. The wire should not be too thick and rigid because then bad distortion is apt to set in. We find 6/10 mil to be the proper thickness, though we also find that different samples of W are likely to vary considerably. The wire used gave a period of about 1/12000 second for a tension corresponding to about $1\frac{1}{2}$ scale marks on the spring of the element and to a sensitivity of about 14 m.a./cm at 1 meter distance. This suspension is difficult to use only on account of the inconvenience of soldering tungsten. Ordinary solder was found proper. The wire is likely to be pulled out of the solder, in which it is held mechanically, at about 2 or 3 scale-divisions tension. The damping was effected by castor oil at room temperature. The magnet of the oscillograph was kept cool by circulating water around it in a rubber tube.

Different values of input resistance were tried for the power amplifier. The dependence of the sensitivity on the value of this was found to be not critical, and 25,000 ohms was found convenient. Two 50,000-ohm grid leaks were used for this in parallel.

A current voltage characteristic of the power amplifier was secured using four tubes. This is drawn in Fig. 3. The good range begins at $E_g = -7$ volts. Connecting the power amplifier in the circuit, it was found that $I_p = 60$ m.a. (i.e., $E_g = -7$ volts) if the grid bias is $+12$ volts. Actually for safety somewhat higher values were used.

Having thus adjusted the power amplifier and oscillograph for no distortion, the voltages on B^+, B_1^+, B_2^+ were varied using laboratory sources of signals and coupling these to the antenna. Two types of sources were used. One consisted of an oscillating receiving tube fed on alternating current in series with some direct voltage and with proper grid bias. By this means short and sharp trains of waves could be obtained. The other was obtained by using a chopper in the plate circuit of the same

oscillator fed on direct current. It was found that B_2^+ at 90 volts or at 67.5 volts is considerably better than at 45 volts, giving better amplification and less distortion. B_1^+ was not very critical, though 22.5 volts was better than O. B^+ was 90 volts. It was found necessary to keep the potentiometer P within safe limits from the oscillation point (1 division on the dial was enough). A badly distorted wave form results otherwise.

In each experiment the deflection at which distortion begins to appear was noted for the particular scale distance used, and the tuning on the oscillator was controlled so as not to exceed such a deflection. The test was usually repeated also during reception by means of visual observations made with a rotating mirror.

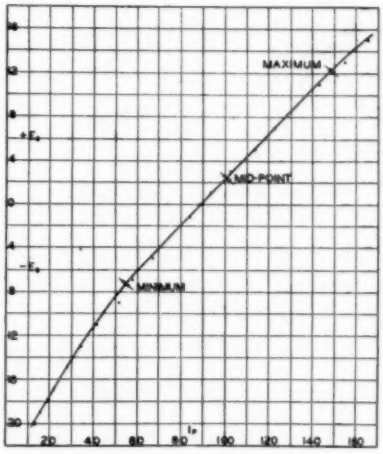


Fig. 3. Current voltage characteristic of power amplifier.

The camera used for recording the wave form was kindly loaned to us by the Sound Section of the Bureau of Standards. The circumference of the drum was about 4 feet and 8 inches. By means of proper relays the drum could be made to spiral on a worm while the picture was taken, thus giving a total length of the record equivalent to three or four revolutions. In the later stages of the work we found it more useful, however, to obtain exposures having a duration of about 1/30 second and corresponding to about one sixth of a revolution. For this purpose an exposure timing commutator was mounted on the shaft of the drum, and the electromagnetic clutch imparting to the drum its translational motion was discarded. The commutator breaks contact when the insulated portion of the commutator drum passes the brush. This corresponds to a definite azimuth of the camera drum. A second commutator is geared

to the main one in the ratio of 8 : 1. The two are connected in parallel, and so the circuit is broken only if the brushes of the two are simultaneously insulated. The commutators are shown as C_1, C_2 on Fig. 4. A short circuiting switch S and a resistance R_1 are also connected as shown. The battery B and the resistance R_2 maintain a difference of potential between P_1 and P_2 which can be varied by adjusting R_1, R_2. With P_1, P_2 as terminals the whole combination is put in series with the grid bias of the power amplifier. With S closed the commutators have no influence. With S open and S' open the oscillograph spot is jerked at every revolution of C_1. The camera is placed so that when C_1 is open the spot is in its range, the adjustment being made with S' open. Next S' is closed. The spot hits the shutter only once in every revolution of C_2. When the brush on C_2 approaches the segment, the shutter is opened,

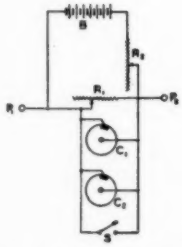


Fig. 4. Connections of exposure timing commutator.

the spot is watched and after it entered the opening, the shutter is closed exposing about one sixth of the film in a particular and known azimuth. The brush on C_1 is then moved into the next position and the last procedure is repeated. Two brushes are provided on C_2 so as to enable all segments to take complete pictures.

The whole drum could be moved also by means of proper stops giving another set of six exposures on another band of the film.

We found it useful for best definition of the pictures to add a second cylindrical lens to the customary optical system. The axis of this was vertical, and it was inserted between the oscillograph mirror and the camera.

The films used were of the Eastman high speed NC type.

Results of Transmission Experiments

(a) *WSC, Tuckerton, N. J.*, Radio Corporation of America. These experiments were of a preliminary nature. In the first tests the Western Electric cathode ray oscillograph was employed. It is provided with two

sets of deflecting plates. One of them was connected directly to the output of the second detector of the superheterodyne set, no further amplification proving necessary. The other set of plates was connected to an alternating potential of adjustable frequency. The cathode beam was also subjected to the action of a magnetic field of the same adjustable frequency, the arrangement being such as to spread the image on the screen into an ellipse, the deflection due to the signal being applied perpendicularly to the major axis. This gave a uniform time scale in the central portion. The source of the adjustable frequency was a shunt-wound motor provided with collector rings which collected, therefore, an approximately sinusoidal current. This was passed through a transformer serving partly as a filter, and the output of the transformer was applied to two coils, one serving as a primary and the other as a secondary of a second transformer. The potential difference across the second secondary was applied to the deflecting plates and the magnetic field of the combination produced a deflection in a perpendicular direction. A rheostat in the field of the motor served to adjust its frequency to synchronism with a submultiple of the frequency of the signal modulation. The figure on the fluorescent screen could thus be kept stationary and inspected.

The modulation at *WSC* was produced by means of a chopper in the grid circuit of the master oscillator with a frequency of about 600 in these as well as later tests, this being one of the commercial methods of transmission used by *WSC*. The frequency of the auxiliary adjustable displacement was about 60, thus giving about 5 humps on each of the two sides of the ellipse. The tests took place at about 9 A.M. in the spring of 1925, the transmission being on 600, 650, or 675 meters with 5 k.w. No definite indication of reflection was obtained in these.

The cathode ray oscillograph was later replaced by the power amplifier and the General Electric oscillograph, so as to obtain photographic records. The apparatus was essentially that described in the first part of the paper except that the modifications in the oscillograph element had not been made at the time, the standard silver suspension and the ordinary method of attaching this being used.

In some cases effects similar to those which would result from reflections were observed. However, they were not very consistent. Samples of various wave forms are shown in Fig. 5.

In order to decide on the conclusiveness of these experiments, a trip to Tuckerton was made and the wave form of the signals was observed by coupling a detector tube to the power amplifier of the transmitter, the output being connected to the power amplifier. These tests showed

that the wave form emitted depended to a large extent on the operation of the chopper and that all the effects observed in Washington could be explained as due to the defective operation of the chopper. (This operation is, of course, quite satisfactory for commercial purposes.) On account of the uncertainty of the emitted wave form, we do not regard these tests as conclusive.

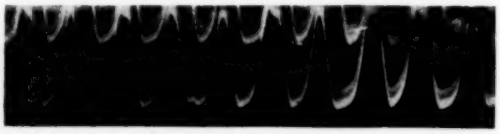


Fig. 5. Wave forms of WSC, Tuckerton, N. J.; $\lambda = 600$ meters; modulation frequency, 600; type of modulation, chopper.

(b) *KDKA, Pittsburgh, Pa.*, Westinghouse Electric and Manufacturing Company. The tests took place in July, 1925, on 309 meters with 10 k.w. The modulation was made by means of 60-cycle plate voltage supply. The interest of these lies in the fact that the transmission took place at night under conditions showing very pronounced fading. Some photographed wave forms are given in Fig. 6. We should like to call attention to the general distortion in the wave form which may be described as fading of very high frequency and also to the small consistent hump which appeared in one instance. This may be due to two-

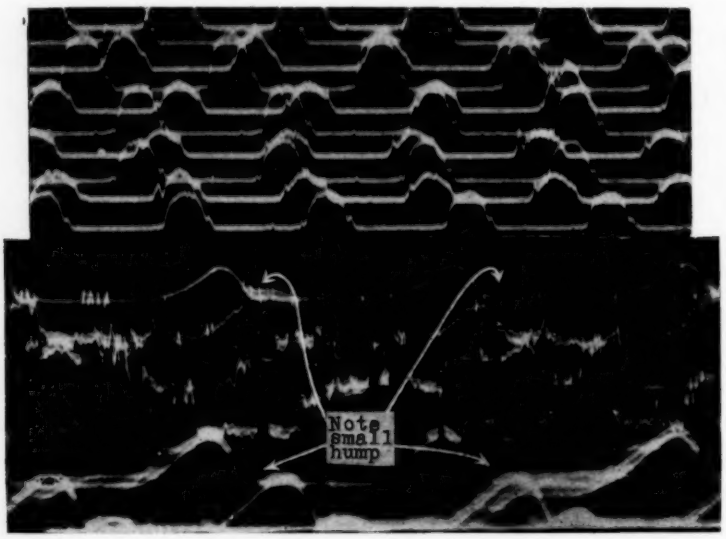


Fig. 6. Wave forms of KDKA, Pittsburgh, Pa.; $\lambda = 309$ meters; modulation frequency, 60; type of modulation, A.C. on plate.

path transmission. However, the fading of *KDKA* is so pronounced and the intensity during the day is so low that we are inclined to look at the main hump as also a reflected one.

(c) *NKF, Bellevue, Anacostia, D. C.*, United States Navy, located 8 miles southeast of the laboratory of the Department of Terrestrial Magnetism. Tests were made on 71.3 meters, 41.7 meters, and unsuccessful ones on shorter waves. These were begun on 71.3 meters on July 28, 1925. The first test (10^h 30^m to 10^h 50^m A.M.) showed double humps with very pronounced fading of one of them. At times a third hump could be seen. The photograph showed only one reflection (two humps). The test was repeated in the afternoon (3^h 15^m P.M.). Three humps were observed in a rotating mirror and also photographed. Shortly afterwards a thunderstorm followed. The appearance of double reflections from Bellevue in several instances which followed was also accompanied by a thunderstorm. In the first two tests the wave form of the transmitter was not perfect, showing a very slight second hump at the transmitter as previously mentioned. Through the kind cooperation of Dr. A. H. Taylor and his assistants this hump was removed by proper biasing of the tubes. On August 6 simultaneous observations were made at Bellevue and at the receiving station of the Department of Terrestrial Magnetism in the intervals from 10^h 30^m to 10^h 50^m A.M. and 1^h 45^m to 2^h P.M. The wave form of the transmitter was perfect all the time, while the wave form at the Department showed a varying second hump in the first period and a constant one in the second.

Fading and Polarization Effects on Bellevue

Since according to the hypothesis one of the humps is due to the direct overground transmission and the others are due to reflections, we should expect that all the humps will be received with different relative effectiveness on different aerials. This proved to be the case. The hump which showed a constant amplitude was received best on a nearly vertical antenna, while the others were received best on antennas with horizontal portions. A number of antennas were put up for the purpose. They were connected to switches so as to be able to shift conveniently from one to the other or to a combination used in parallel. Invariably changing antennas produced changes in relative intensities. At the same time no effect on the wave form due to tuning on the superheterodyne oscillator could be observed, thus showing that the effect was not due to detuning of the circuits resulting from different circuit constants of the antennas (such effects have been observed with other transmitters to be described presently). These observations confirm our interpretation of the hump

with a constant amplitude as a direct transmission effect. Other quite direct evidence of this interpretation will be given in a later section.

Since the reflected wave must be coming down to the ground, we should expect it to form an *interference pattern* at the surface. If the wave should be coming directly down and if the ground should behave as a perfect conductor, we should expect a node of the electric intensity at the ground and a loop at a height equal to a quarter of a wave-length. We have some indications to that effect. Three antennas stretched east with horizontal portions at about 6, 30, and 50 feet above ground, respectively, indicated that the reflection is received strongest by the antenna of medium height. The two others show the reflection weaker to about the same extent. We can perhaps take 30 feet to be approximately the position of the loop of the interference pattern. The wave-length being 71.3 meters, one quarter of it is 17.8 meters = 58 feet. Hence the angle which the wave would appear to make with the vertical would be $\cos^{-1}30/58 = 60°$. It is hardly correct to attach any significance to this estimate except as a purely qualitative one on account of the interaction of the antennas, the effect of the buildings, the small number of antennas used, etc.

We have also observed the wave form by means of a loop inside the building. The relative intensity of the two waves changed markedly on turning the loop. We do not feel justified in making any interpretation of the actual relations on account of the effects of surrounding objects.

In most of the experiments, with few exceptions, the hump showing variations showed them very markedly. At times these were very rapid (1 or 2 seconds), at others slower (10 to 15 seconds), and in others quite slow (steady for several minutes). The variations in amplitude were very marked, making the reflected wave change from practically zero to the amplitude of the ground wave and sometimes higher. This shows that fading can exist quite apart from interference between ground and reflected waves and that a considerable part of it is due to the different effectiveness of reflection. The great variability of the intensity of reflection suggests either that the reflection itself is governed by interference phenomena or that it is caused by sudden changes in the layer more or less as the flickering of a light on a wavy surface of water. We have no evidence to decide between these points of view. The existence of multiple reflections can perhaps be seen more easily on the hypothesis of a wavy surface in the layer.

Identification of the Waves

Although the intensity of the reflected wave varied considerably, there have been many cases in which it remained definitely below the intensity

of the ground wave. In these cases photographs showing the beginning or the end of a dot or dash enabled us to identify the waves because the first hump must be always received along the shortest path and the last along the longest. Some such photographs are reproduced among the others of Fig. 7. They confirmed our previous opinion as to the identity

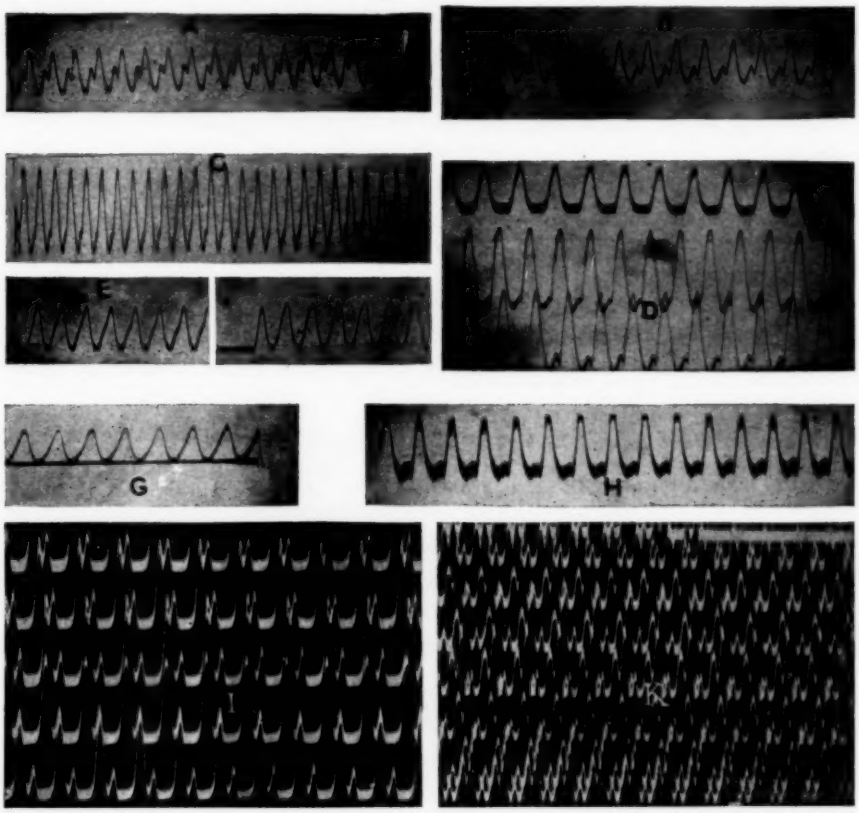


Fig. 7. Wave forms of NKF, Bellevue, Anacostia, D.C.; $\lambda = 71.3$ meters; modulation frequency, 424; type of modulation, A.C. on plate.

(A) Identification of ground and reflected waves at end of transmission, September 25, 1925, 3:30 P.M.
(B) Identification of ground and reflected waves at beginning of transmission, September 25, 1925, 3:30 P.M.
(C) September 25, 1925, 1:30 P.M.
(D) September 25, 1925, 1:30 P.M.
(E) Superposed and interfering waves, September 25, 1925, 3:30 P.M.
(F) Another stage of superposition and interference resulting in approximately sinusoidal wave form, September 25, 1925, 3:30 P.M.
(G) Third stage of distortion due to superposition and interference.
(H) "Multiple reflections," September 21, 1925, 3:30 P.M.
(I) Single reflection with low position of layer, July 28, 1925, 10:35 A.M.
(K) Double reflection, July 28, 1925, 3:15 P.M.

of the humps. It must be noted that in pictures with good focusing such as (A) the shape of the reflected hump is the same as that of the ground hump except for a scale factor representing the intensities.

EFFECT OF WAVE-LENGTH, TIME OF DAY, AND LOCATION OF RECEIVER

Signals on 71.3 meters showed reflections when received at the laboratory of the Department of Terrestrial Magnetism in a great majority of cases. On 41.7 meters at $10^h\ 30^m$ A.M. a number of tests in August and September failed to show reflections. However, in the afternoon at $3^h\ 30^m$ P.M. a marked change in the wave form was found (Fig. 8). It is more irregular than that on 71.3 meters. On the whole, reflections on 71.3 meters are more marked in the afternoon than in the morning.

Fig. 8. (A) Wave form of NKF; $\lambda = 41.7$ meters; modulation frequency $\simeq 500$; shows original wave form, September 29, 1925, 10:30 A.M.
(B) Wave form of NKF; $\lambda = 41.7$ meters; modulation frequency $\simeq 500$; wave form badly broken and visual observations showed rapid and irregular changes, September 29, 1925, 3:30 P.M.

Special arrangements for transmission were made for December 11, 12, 13, 1925, in connection with the annual exhibit of the Carnegie Institution of Washington. The receiving apparatus was moved about 3 miles towards the transmitter (Sixteenth and P Streets, Northwest), the distance being about 5 miles from *NKF* and 2.5 miles from *WWV*. Here also reflections were observed, though weaker than at the laboratory. No specially marked effect of reception in the evening was observed ($9^h\ 30^m$ to $9^h\ 45^m$ P.M.).

No reflections were observed on 20 meters or shorter wave-lengths.

(d) *WWV, Bureau of Standards*, Washington, D. C. The two laboratories being very close together (1.2 miles), only a weak reflection could be expected. Transmission took place on 75 meters and 50 meters with 500 cycles as well as 60-cycle modulation. The modulation was effected by means of the usual alternating-current method. However, the set was not crystal controlled, and therefore it did not show a constant frequency during a modulation cycle. This led at first to absurd results giving an apparent change of wave form due to the sharp tuning of the superheterodyne. This change of wave form can be at times confused with a reflection. We made sure that it was not a reflection by oscillographing *WWV* in its own building using the same superheterodyne set

and power amplifier. In such a way it was made sure that the effect of Fig. 9 is a detuning effect. However, it appears that with 500-cycle modulation the effect of detuning is not so important, and apparently a real reflection has been observed (Fig. 10). The height of the layer from this film agrees with that obtained from Bellevue.

Effects like the one shown in Fig. 9 have been observed by Bown, Martin, and Potter.[2]

Fig. 9. Wave form of WWV; $\lambda = 50$ meters; modulation frequency $= 60$; type of modulation, A. C. on plate; wave form badly distorted due to frequency change in transmitter, November 10, 1925, 3:30 P.M.

Fig. 10. Wave form of WWV; $\lambda = 50$ meters; modulation frequency $= 780$; November 10, 1925, 3:30 P.M.

Discussion of Results

Measurements of the films obtained on Bellevue give values of the height which seem to vary with the time of year and with the time of day. The latter variation is not certain. The speed of the 500-cycle machine used in the transmitter was measured by means of a revolution counter and was found to be 26.4 revolutions per second. The machine had 32 inductors and two poles giving a frequency $= 424 \frac{\text{cycles}}{\text{sec.}}$. This was also checked by means of a whistle borrowed from Mr. Mirick of the Naval Research Laboratory and calibrated by him against standard tuning forks. A mean of 12 observations gave for the frequency $425 \frac{\text{cycles}}{\text{sec.}}$ If we should deal with a case of pure reflection taking place in the zenith, we must have

$$\frac{2h}{c} = \Delta t$$

where h is the height of the layer, c the velocity of light, and Δt the time elapsed. If a is the ratio of the distance of the peak of the reflected wave from its parent ground wave to the distance between two ground waves on the oscillogram, we have $\Delta t = \frac{a}{435}$ and with $c = 186{,}000 \frac{\text{miles}}{\text{sec.}}$

$$h = 196\ a \text{ miles}$$

In such a way we calculate from measurements on our photographs for h the results shown in Table I.

[2] Ralph Bown, De Loss K. Martin, and Ralph K. Potter, Bell System Tech. J. 5, 143–213 (1926).

TABLE I

Height of the reflecting layer

Date	75th meridian time	Resulting height, h	Remarks
1925	*h m*	*miles*	
July 28	10:35 A.M.	55	
	3:45 P.M.	55	For strong reflection.
		141	For weaker reflection.
Sep. 21	10:30 A.M.	118	
	11:30 A.M.	117 (80?)	Identification of ground and reflected waves not quite certain.
	1:30 P.M.	125	
	3:30 P.M.	91	For weaker reflection.
		125	For stronger reflection.
		125	When reflection became single.
Sep. 23	10:30 A.M.	106	
	1:30 P.M.	116	
	3:30 P.M.	132	
Sep. 25	10:30 A.M.	79	
	11:30 A.M.	106	
	1:30 P.M.	120	
	3:30 P.M.	125	

These values are recorded more accurately than they can be relied upon. The accuracy of measuring the films is probably 5 percent and in bad cases 10 percent. The speed of the generator could also vary on account of fluctuations in the line voltage by perhaps 2 percent. However, it seems that in the afternoon the layer is higher than in the morning, and with more certainty that in the fall it is higher than in the summer.

From the Bureau of Standards the only film available for measurement gave 80 miles in an afternoon in November. However, we do not rely on this as much as on the results from Bellevue.

It must be pointed out that the "height" which we have tabulated is in reality only a retardation and that we cannot compare it directly with the results of Taylor and Hulburt.[3] In all probability the mechanism involved in producing the "reflected" hump is more similar to refraction than reflection. We must therefore take into account the change of velocity of the waves in the refracting medium. We consider in this connection the group velocity of the waves. If $V(\nu)$ should be the phase velocity for a frequency ν, the group velocity is

$$V' = \frac{d\nu}{d\left(\frac{\nu}{V}\right)} = \frac{V}{1 - \frac{\nu}{V}\frac{dV}{d\nu}} \tag{1}$$

[3] A. H. Taylor and E. O. Hulburt, Phys. Rev. **27**, 189(1926).

For an *ordinary* dispersing medium we may take

$$V = c\left[1+\frac{\alpha}{\nu_0^2-\nu^2}\right]^{-\frac{1}{2}} \quad (\alpha>0) \tag{2}$$

This gives

$$V' = c\left[1+\frac{\alpha}{\nu_0^2-\nu^2}\right]^{\frac{1}{2}}\left[1+\frac{\alpha\nu_0^2}{(\nu_0^2-\nu^2)^2}\right]^{-1} \tag{3}$$

In order that $V'<c$ we must have

$$\frac{\alpha}{x} < \frac{2\alpha\nu_0^2}{x^2}+\frac{\alpha^2\nu_0^4}{x^4} \tag{4}$$

where $x=\nu_0^2-\nu^2$.

The most important case for us is that of $\nu>\nu_0$, i.e., $x<0$ and $V>c$. It is also always true for $x>0$ because the maximum value which x may have corresponds to $\nu=0$, i.e., $x=\nu_0^2$. In the case (4) becomes $a<2a+a^2/\nu_0^2$ which is always true. Thus the group velocity is always $<c$, and hence in spite of the greater phase velocity in the upper regions the effective path-difference for our experiment is greater than the geometrical. This tends to make all of our measurements give too large values of h.

The values of h are also likely to be too large on account of a possible oblique direction of the ray. For a real determination of the height, the direction in which the waves come down would have to be measured and one would have to make sure that if the emitted radiation be confined to that direction the reflected wave will exist. Otherwise multiple successive reflections will have to be assumed.

Again, a direct comparison with skip-distance data is not warranted because the skip-distance observations do not give directly the height and are likely to give too high values for the penetration of the waves into the upper regions. Further, in the measurements of skip distances the properties of the layer over a greater range are important, and casual prominences of interest to us may be of no importance in the other case.

The more sudden the transition to the region of strong ionization the less chance there is of error due to the difference between V' and c. Also the greater the angle which the ray makes with the layers of equal refractive index the less is that chance. The reason for this is that formula (3) may be written as

$$V' = \frac{c\mu}{1+\dfrac{\nu_0^2}{\nu_0^2-\nu^2}(\mu^2-1)}$$

which shows that if $\mu=0$, $V'=0$, so that if the wave penetrates the region in which $\mu=0$, there will be a large retardation. If the layers of equal electron density should be horizontal

$$\mu \sin\theta = \text{const.}$$

where μ is the refractive index and θ is the angle which the wave normally makes with the vertical. If the initial value of θ is 0, the highest point in the path is reached when $\mu=0$.

Quite similarly to the manner in which we have used (2) to derive (3) we may use the various expressions for the refractive index employed by Taylor and Hulburt and given in their expressions (2), (3), (5), (6). Corresponding to them we have for circularly polarized rays propagating along the field

$$V(\nu) = c\left[1+\frac{\alpha}{\nu(\nu_0-\nu)}\right]^{-\frac{1}{2}} \tag{5}$$

or

$$V(\nu) = c\left[1-\frac{\alpha}{\nu(\nu_0+\nu)}\right]^{-\frac{1}{2}} \tag{6}$$

and if the wave propagates perpendicularly to the magnetic field for polarization parallel and perpendicular to the field respectively

$$V(\nu) = c\left[1-\frac{\alpha}{\nu^2}\right]^{-\frac{1}{2}} \tag{7}$$

$$V(\nu) = c\left[1-\frac{\alpha\nu^{-2}}{1-\frac{\nu_0^2}{\nu^2}(1-\alpha\nu^{-2})}\right]^{-\frac{1}{2}} \tag{8}$$

Here $\alpha=Cc^2$ where C is the same as that used by Taylor and Hulburt. Corresponding to these expressions we have refractives indice μ given by

$$\mu^2-1=\frac{\alpha}{\nu(\nu_0-\nu)} \tag{5'}$$

$$\mu^2-1=-\frac{\alpha}{\nu(\nu_0+\nu)} \tag{6'}$$

$$\mu^2-1=-\frac{\alpha}{\nu^2} \tag{7'}$$

$$\mu^2-1=-\frac{\alpha\nu^{-2}}{1-\frac{\nu_0^2}{\nu^2}(1-\alpha\nu^{-2})} \tag{8'}$$

Remembering that $V(\nu)=\dfrac{c}{\mu\nu}$ we find easily that

$$V'(\nu) = \frac{d\nu}{d\left(\frac{\nu}{V(\nu)}\right)} = \frac{c\mu}{\mu^2 + \frac{\nu}{2}\frac{d\mu^2}{d\nu}} = \frac{c\mu}{1+(\mu^2-1)\left\{1+\frac{\nu}{2}\frac{d\log(\mu^2-1)}{d\nu}\right\}} \tag{9}$$

This gives for the four cases

$$V'(\nu) = \frac{c\mu}{1+\frac{\nu_0}{2(\nu_0-\nu)}(\mu^2-1)} \tag{5''}$$

$$V'(\nu) = \frac{c\mu}{1+\frac{\nu_0}{2(\nu_0+\nu)}(\mu^2-1)} \tag{6''}$$

$$V'(\nu) = c\mu \tag{7''}$$

$$V'(\nu) = \frac{c\mu}{1-\frac{\mu^2+(\mu^2-1)\left(1-\frac{\nu_0^2}{\nu^2}\right)}{\frac{\nu^2}{\nu_0^2}-1}(\mu^2-1)} \tag{8''}$$

It is seen most clearly in the case (7'') that if $\mu=0$, $V'=0$. We must therefore pay attention to the retardation which the group receives in the highest points of the path because there the velocity of the group is very small. The retardation is given in general by

$$\Delta t = \int \frac{ds}{V'} \tag{10}$$

Here we can write

$$ds = \frac{dx}{\sin\theta}$$

and

$$\mu \sin\theta = K = \sin\theta_0 \tag{10a}$$

where K is constant for a given path. Hence

$$\Delta t = \int \frac{\mu}{V'K}\,dx \tag{11}$$

For (7'') this becomes

$$\Delta t = \frac{\Delta x}{c\sin\theta_0} \tag{12}$$

This shows that the measured retardation for transmission along a curved path ABC (Fig. 11) is the same as that which would take place in vacuo along ADC where AD, CD are tangent to ABC at A and D. In this case, therefore, the result depends on somewhat the same type of extrapolation as in the case of skip-distance determinations of the height. If one should be able to perform the reflection experiment with the base line about equal to the skip distance and if one should determine the direction of the downcoming wave at the skip distance, a close agreement for the reflection corresponding to (7) would be expected.

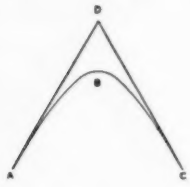


Fig. 11. Relation of actual path to the effective one.

Formula (11) when applied to the cases marked (5), (6), (8) gives for (5)

$$\Delta t = \frac{\Delta x}{c \sin \theta_0}\left\{1 + \frac{\nu_0}{2(\nu_0 - \nu)}\ \overline{(\mu^2 - 1)}\right\} \tag{13}$$

for (6)

$$\Delta t = \frac{\Delta x}{c \sin \theta_0}\left\{1 + \frac{\nu_0}{2(\nu_0 + \nu)}\ \overline{(\mu^2 - 1)}\right\} \tag{14}$$

for (8)

$$\Delta t = \frac{\Delta x}{c \sin \theta_0}\left\{1 - \overline{(\mu^2-1)\left[\mu^2+(\mu^2-1)\left(1-\frac{\nu_0^2}{\nu^2}\right)\right]}\left(\frac{\nu^2}{\nu_0^2} - 1\right)^{-1}\right\} \tag{15}$$

where the averaging indicated by the bar is taken over the path assigning equal weights to portions of the path having equal projections along the horizontal (x). Here if $\nu > \nu_0$ which is the case concerning us (13) gives results $>$ those derived from (12) for the same θ_0. On the other hand, (14) gives values which are smaller while the behavior of (15) depends to a large extent on the nature of the electronic distribution. The largest value which $\overline{1-\mu^2}$ may have is 1. For 70-meter waves $\nu_0/(-\nu_0+\nu)$ is about one half and thus the largest discrepancy between the correction-factors in (13) and (12) which we should expect is that given by a factor 5/4, while (14) is not to be expected to give values of the correction-factor smaller than seven-eighths of those given by (12). Such discrepancies are not negligible and may account ultimately for some cases of multiple reflections, especially if it is remembered that $\sin \theta_0$ is different for all the cases so that ADC of Fig. 11 is also different. It may be also that rapid fading of the reflections is due to interference influenced by changes in the group velocity.

We must consider next the question of possible changes in the group velocity within the band of the transmitter. We see by means of (7″) and (7′) that

$$\frac{dV'}{d\nu} = \frac{\alpha}{\nu^2\sqrt{1-\frac{\alpha}{\nu^2}}} \qquad 16)$$

so that if $\mu=0$, $dV'/d\nu=\infty$. The distortion due to changes in the group velocity would be expected to be infinitely great for rays returned from the zenith if the electronic density in horizontal layers is constant. For 70-meter waves, however, we observed a close reproduction of the original wave form in the reflections. We must explain, therefore, why the distortion does not take place. Various explanations may be given. It may be said that the waves are reflected rather than refracted or else it may be supposed that the electron density is not uniform in horizontal layers so that the region of $\mu=0$ is not reached. Before arriving at any such conclusion, however, we must consider the problem in a more exact quantitative manner.

Let us suppose, for instance, that the electron density increases as the square of the height. Then

$$\alpha = by^2$$

where b is a constant. Hence also for (5′)

$$\mu^2 = 1-\alpha(\nu)y^2$$

where

$$\alpha(\nu) = \frac{b}{\nu(\nu_0-\nu)}$$

Calling the range which the ray spans l

$$l = \frac{\pi\sin\theta_0}{\sqrt{a(\nu)}}$$

and since $\overline{1-\mu^2} = a(\nu)\overline{y^2}$ where

$$y = \frac{\cos\theta_0}{\sqrt{a}}\sin\left(\frac{\sqrt{a}}{\sin\theta_0}x\right)$$

we have

$$\overline{y^2} = \frac{\cos^2\theta_0}{2a} \text{ and } \overline{1-\mu^2} = \frac{\cos^2\theta_0}{2}.$$

Thus (13) becomes

$$\Delta t = \frac{l}{c\sin\theta_0}\left\{1-\frac{\nu_0}{4(\nu_0-\nu)}\cos^2\theta_0\right\}$$

This is the exact retardation of a group of waves having a very small spectral width. Keeping the range l constant, the initial angle θ_o is determined by

$$\sin\theta_0=\frac{l}{\pi}\sqrt{\frac{b}{\nu(-\nu_0+\nu)}} \tag{17}$$

and the retardation is

$$\Delta t=\frac{\pi}{c}\sqrt{\frac{\nu(-\nu_0+\nu)}{b}}\left\{1+\frac{\nu_0}{4(\nu-\nu_0)}\left[1-\frac{l^2}{\pi^2}\,\frac{b}{\nu(-\nu_0+\nu)}\right]\right\} \tag{18}$$

In the limit if $l=0$,

$$\Delta t=\frac{\pi}{c}\sqrt{\frac{\nu(-\nu_0+\nu)}{b}}\left[1+\frac{\nu_0}{4(\nu-\nu_0)}\right] \tag{18'}$$

We see that neither (18) nor (18′) vary especially rapidly with ν, and hence there is no danger of distortion. In fact it may be shown that the change in the retardation $\delta(\Delta t)$ is of the order of $\Delta t\nu^{-1}\delta\nu$ and is thus very small.

Formula (18) may not be applied if $\nu<\nu_o$ because then $a(\nu)<0$ and its square root is imaginary, nor can it be used if

$$l^2>\frac{\pi^2\nu(-\nu_0+\nu)}{b}$$

because then $\cos^2\theta_o<0$. Formula (18) shows that we should expect a certain variation in the apparent height with the range covered on account of the presence of l. However, in the case of 70-meter waves the variation in retardation is small, amounting to about one eighth of the whole.

With the same electron distribution the circular polarization corresponding to (6′) gives a retardation

$$\Delta t=\frac{\pi}{c}\sqrt{\frac{\nu(\nu+\nu_0)}{b}}\left\{1-\frac{\nu_0}{4(\nu+\nu_0)}\left(1-\frac{l^2}{\pi^2}\,\frac{b}{\nu(\nu+\nu_0)}\right)\right\} \tag{19}$$

It is important to observe that for 70-meter waves (19) is not even approximately the same as (18). Disregarding correction terms in parentheses, their ratio is

$$\sqrt{\frac{\nu_0+\nu}{-\nu_0+\nu}}$$

For 70-meter waves this ratio is approximately 1.4. The fact that in most cases two reflections with such retardation ratios have not been observed speaks for a more sudden increase in the electron density than that given by the $\alpha = by^2$ relation or else for a failure of the simultaneous appearance of the true circular components.

The polarization corresponding to (7′) gives

$$\Delta t = \frac{\pi}{c}\sqrt{\frac{\nu^2}{b}} \tag{20}$$

a value in between the other two.

It is scarcely necessary to state that the first electron distribution used by Taylor and Hulburt gives possibilities of multiple down-coming rays simply because for every range there are two possible rays for every state of polarization. Unless the hypothesis of a wavy lower surface applies, we may also consider the possibility of a general increase of uniformity in electron distribution as an explanation of multiple reflections.

Summary

(1) Groups of radio waves arrive at the receiving station separated from their echoes. This shows that the hypothesis of an ionized upper layer of the atmosphere is correct.

(2) The retardation is such as though the layer were at a height of from 50 to 130 miles. The apparent height is greater in the fall than in the summer for 70-meter waves with an 8-mile base.

(3) Radio fading is present for reflections alone quite independently of interference between the ground and reflected waves.

(4) A quantitative discussion of the possibilities of refraction shows that in most cases the increase of electronic density must be more sudden and discontinuous than that given by a density proportional to the square of the height or else that not all of the possible states of polarization of the waves in the upper atmosphere are present.

The writers are greatly indebted to the various institutions which cooperated in the transmission of signals, particularly so to the Naval Research Laboratory and the Bureau of Standards which has been very generous in loaning apparatus. They also desire to express their sincere thanks to Mr. J. A. Fleming of the Department of Terrestrial Magnetism for his help in making the necessary arrangements and to Mr. C. Huff for the great interest and thoroughness with which he constructed the necessary apparatus.

Department of Terrestrial Magnetism,
Carnegie Institution of Washington,
May 19, 1926.

MAGNETIC MOMENTS OF THE ALKALI METAL ATOMS

By John B. Taylor.[1]

Abstract

The work of Stern and Gerlach in which they determined the magnetic moments of certain atoms and at the same time furnished direct evidence of the theory of space quantization, by deflection of rays of the atoms in an inhomogeneous magnetic field, has been repeated for silver atoms. A simplified apparatus is described, using a silver plated tungsten coil as source of atoms, rather than the furnace used by Stern and Gerlach, which gives trouble in outgassing.

The magnetic moment of sodium and potassium. The apparatus was further modified for use with the alkali metals by construction of a liquid air cooled target for receiving the atomic rays and a Pyrex glass device for holding the molten metal during evaporation. The images of the rays on the glass target were made visible by immersing in hydrochloric acid gas, which "fixed" them as the opaque and visible chloride. Distinct images of the separated rays resulting from the action of the magnetic field on the oriented atoms have been obtained and are reproduced. Measurements of the separations show that, within the experimental error, sodium and potassium possess magnetic moments equal to one Bohr magneton, in accord with spectroscopic predictions.

THE experiments of Stern and Gerlach,[2] in which they determined the magnetic moments of certain atoms by deflection of a ray of the atoms in an inhomogeneous magnetic field, have introduced a method of research of great interest. Measurements of susceptibilities and observations on magneto-mechanical systems both deal with matter in bulk, where the effects of the solvent and of neighboring atoms cloud the results. The "atomic ray" is a uni-directional narrow beam of atoms in which there is little or no inter-collision effect. This allows investigation of the action of individual atoms, and it is with such rays that Stern and Gerlach have secured direct evidence of space quantization and a direct measure of the unit of magnetic moment so far accepted,—the Bohr magneton.

The equation relating the amount of deflection of the atomic ray to the magnetic moment of the atom is:

[1] This communication is an abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] O. Stern, Zeits. f. Physik., **7**, 249 (1921); W. Gerlach and O. Stern, Zeits. f. Physik. **8**, 110 (1921); **9**, 349, 353 (1922); Ann. d. Phys., **74**, 673 (1924); **76**, 163 (1925).

$$\frac{1}{M} = \frac{1}{2s}\left(\frac{\partial H}{\partial s}\right)_0 \frac{l^2}{3.5RT}\left\{1 + \frac{l^2 M}{12 \times 3.5RT \times s}\left[\left(\frac{\partial H}{\partial s}\right)_l - \left(\frac{\partial H}{\partial s}\right)_0\right]\right\}$$

Here s is the amount of deflection measured as shown later; M is the magnetic moment (gauss cm per mol.); l is the length of the pole pieces of the magnet, the distance the atomic ray must travel through the magnetic field; $(\partial H/\partial s)_0$ is the value of the inhomogeneity of the field at the point where the ray enters the field; $(\partial H/\partial s)_l$ is the corresponding inhomogeneity at the end of the field, after the deflection of the ray. This is not equal to $(\partial H/\partial s)_0$ since $\partial H/\partial s$ changes in value from point to point across the field between the pole pieces, being greatest next to the knife edged pole piece. (See below.) The values of $\partial H/\partial s$ are obtained for any distance of the ray from the knife edge by a preliminary mapping of the field. The 3.5 RT term comes from the expression which Stern[3] found in his direct measure of the velocity of the silver atom.

Since the work of Stern and Gerlach appears to be of such fundamental importance, it was thought desirable to repeat it in way of confirmation, and if possible to extend it. Their initial experiments in which they found the normal silver atom to possess a magnetic moment equal to one Bohr magneton have been repeated in a simplified apparatus. Following this, the alkali metal atoms, sodium and potassium, have been investigated.

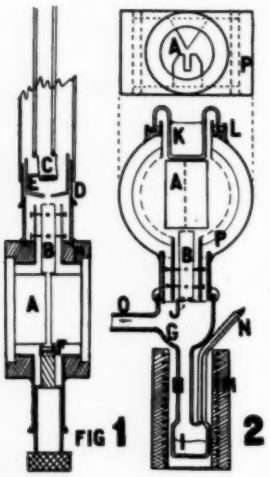
Experimental

A large Dubois type magnet, possibly a duplicate of Stern and Gerlach's, was used to produce the magnetic field. The apparatus for formation, deflection, and detection of the atomic rays was suspended between the flat pole pieces of this magnet. It was a vacuum tight brass box with end tubes, as shown in three sections at P, in Figs. 1 and 2. The auxiliary pole pieces for producing the inhomogeneous field were of soft iron, shaped as at A and held on soft iron plates set in and soldered to shoulders on the brass box. One pole piece was a 60° knife edge, the other slotted as shown in the upper view of Fig. 2. Magnetic measurements showed the field produced and the inhomogeneity of the field to be closely that used by Stern and Gerlach. (See also below.)

Fig. 1 gives one section of the brass box P, and the arrangement for silver. Fig. 2 gives other sections of P, but the arrangement is for the alkali metals as will be described later. In Fig. 1, C is a silver plated tungsten coil which was a source of silver atoms when heated by passage of current. The silvered coil gives less trouble in outgassing than does a

[3] O. Stern, Zeits. f. Physik., **2**, 49 (1920).

small furnace of the type used by Stern and Gerlach. It was suspended on long copper leads sealed out through copper tubes, which in turn were sealed through a Pyrex head piece (not shown). A ground joint allowed removal of this head piece with the coil for replating with silver. It also carried a plane glass plate to allow control of the temperature with an optical pyrometer. This temperature was held at approximately 1200°K. The Pyrex glass tube supporting the coil holder was sealed to a short thin walled copper tube D, which was soldered to the brass box.



Figs. 1 and 2. Diagram of apparatus.

The slits, which form the ray, were made in thin copper disks held on a framework and adjusted by a set of screws as shown at B. The slits used in the experiments with silver were both .1 mm wide, 2mm long, and held 3 cm apart. The slits must be adjusted so that the path of the atoms, after leaving them, will be exactly parallel and at the desired distance from the knife edged pole piece. Between the coil and the first slit a glass diaphragm E was inserted to prevent silvering the whole interior of the apparatus.

The ray of silver atoms was received on tiny glass plates held under a cap on the plate holder, as shown at F in Fig. 1. The surface of the plate was less than a millimeter from the end of the pole pieces. The time of run was usually about one hour, during which time a vacuum of $3-5 \times 10^{-5}$ mm was maintained in the apparatus. At the end of the run the plate holder was removed and the glass plate, bearing an invisible image of the silver atoms on its face, was immersed in a dilute (one percent)

hydroquinone-silver nitrate intensifying bath.[4] This deposited more silver upon the trace already there and made the image visible for measurement.

The images obtained for silver did not show a splitting or separation into two lines as obtained by Stern and Gerlach. This was undoubtedly because the slits were too wide in proportion to the amount of deflection to show more than a decided broadening of the ray in the magnetic field. A trace of division was noticed in some of the runs. These results indicated that the apparatus was in working order and the investigation of the alkali metals was begun.

The apparatus was modified as shown in Fig. 2. A Pyrex container *G* held the alkali metal. This container consisted of a pot *I*, short tube *H* for limiting the evaporation of the metal from *I*, and an enlargement above *H* for sealing with de Khotinskey cement to the brass box *P*. The box is shown inverted in this figure, since the alkali metals were evaporated from below,—not from above as for silver in Fig. 1. The capillary *N* is for filling. *O* leads to liquid air trap, McLeod gage and pumps.

After a preliminary test of the apparatus by pumping to a high vacuum, the capillary was blown out at *N*, and the filling device sealed on. This was a series of small bulbs connected by tubes or short lengths of capillary, and allowed successive distillation and filtration of the alkali metal completely in vacuum. The metal reached *I* in a mirror like condition and after a short heating was practically gas free. A residual gas pressure averaging 4×10^{-5} mm was held during the runs. *M* is a copper tube furnace for heating the metal in *I* and the tube *H*. Temperatures were read with a chromel alumel couple calibrated under the conditions of the experiment. *J* is a copper diaphragm which prevented alkali metal from entering the pole piece box and carried a small iron shutter which closed the opening of the diaphragm during outgassing, to avoid unnecessary clogging of the fine slits.

A run was started by applying the magnetic field. This opened the iron shutter, which had been suitably oriented, and the slits were thus exposed to the stream of atoms. The atomic rays were in this case received on a Pyrex target *K* whose face was cooled by liquid air. Definite images could not be secured on uncooled targets. The use of this target necessitated a change, as shown, in this end of the box *P*. The tube and plate holder *F* were replaced by the Pyrex target *K* and the circular brass channel *L*, which allowed easy insertion and sealing of the target with beeswax rosin mixture.

[4] J. Esterman and O. Stern, Zeits. f. Phys. Chem., **106**, 399 (1923).

The images, sodium or potassium, were made visible by immersing the target in hydrochloric acid gas. This "fixed" the images as the opaque and visible chloride.

The first slits used were 0.1 mm×2 mm, and as for silver gave only broadened images. (See Plate I.) Then in a series of runs and adjustments the slits were narrowed gradually to a width of .03 mm, when images as shown in Plates II, III, and IV were obtained.

Sodium was evaporated at 345°C and potassium at 245°C.

Discussion of the Images and Calculations of the Magnetic Moments

The Plates I–IV are photomicrographs of the original tiny images. Plate I (16×) for sodium, shows only the broadening and is unsuitable for measurement.

Plates II and III (16×), show the divided rays finally obtained for sodium and potassium. Plate II was unfortunately formed on a target streaked with bubbles in the glass. Under the microscope it was almost as clearly defined as III. Plate IV is a photomicrograph (32×) of the splitting shown in III.

Fig. 3 is a diagram of Plate III with dimensions. The distance s is the quantity used in the calculation of M, the magnetic moment. The location of the outer limit of s, at the most dense point in the branch of

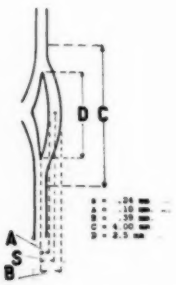


Fig. 3. Diagrammatic sketch of Plate III.

S = .24 mm
A = .10 mm
B = .39 mm
C = 4.00 mm
D = 2.5 mm

the split, is easily seen under the microscope. The measurements were made with an eye piece micrometer. At X the image (see also III) appears to be pulled out and flattened. This is the side toward the knife edge and has actually been drawn against the pole piece by the greater

$\partial H/\partial s$ at the edge. For this reason the more uniformly deflected branch of the split is chosen for measurement of s.

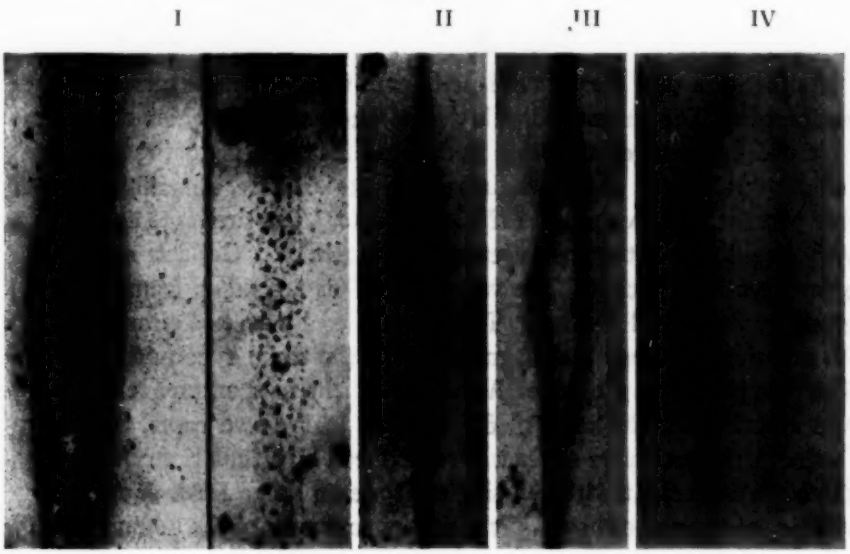


Plate I. Sodium. (A) without field; (B) with field, broadened only.
Plate II. Sodium. Plate III. Potassium. Plate IV. Potassium.

The data for calculation of M from these images are as follows: Slits, $.03 \times 2.5$ mm; pole piece, length, 3.0 cm; distance, middle of slits from knife edge, 0.26 mm; giving $(\partial H/\partial s)_o$ a value of 160,000 gauss per cm.

Sodium $s = 0.20$ mm $(\partial H/\partial s)_l = 105{,}000$. $T = 620°\text{K}$

Potassium $s = 0.24$ mm $(\partial H/\partial s)_l = 94{,}000$. $T = 520°\text{K}$

By inserting these values of s $(\partial H/\partial s)_o$, $(\partial H/\partial s)_l$, l and T in the equation given above, there results for the magnetic moments:

$M = 5350$ gauss cm, from the data on sodium.

$M = 5380$ gauss cm, from the data on potassium.

This is about a four percent difference from 5584, the Bohr unit magneton value, and warrants the conclusion that normal atoms of sodium and potassium both possess a magnetic moment equal to one Bohr magneton.

An examination of the equation shows that the deflection s is independent of the atomic weight of the element and that elements of equal magnetic moment should have s related inversely as the absolute temperatures of evaporation.

$$s_{\text{Na}}/s_{\text{K}} = .20/24 = .833; \qquad T_{\text{K}}/T_{\text{Na}} = 520/620 = .838$$

The single magneton value for the alkali metals is in accord with the spectroscopic prediction made possible by use of Landé's[5] classification of the anomalous Zeeman effect, as referred to the neutral unexcited atom.

Accuracy

As in Stern and Gerlach's experiments the possible error is close to ten percent. The largest source is the measurement of s, which on account of the diffuseness of the lines and the difficulty in judging the exact points of reference, can be measured only to .01 mm, a possible error of five percent. The values of $(\partial H/\partial s)_o$ and $(\partial H/\partial s)_l$ are large and do not vary rapidly, yet the measurements of Stern and Gerlach may be in error by a few percent. The values of $\partial H/\partial s$ are taken from the table given by Stern and Gerlach. This is justified by several circumstances. As mentioned before the magnets are of the same type and capacity. The pole pieces are the same. Also by using the temperature relationship and allowing for the ratio of $\partial H/\partial s$ used in the two cases, Stern and Gerlach's deflection for silver was reproduced by calculation. Moreover, the close agreement with the single magneton value 5584, supports the validity of the value chosen. Precise measurements of the inhomogeneity are now being made but will be of no advantage until the large error in the measurement of s is removed. It is important to note that this error in $\partial H/\partial s$ can be practically eliminated by choice of a reference substance giving a certain s under set conditions of the slit system. Temperatures were read to within one percent.

It is seen that the reduction of the possible error in these experiments is an important matter, and that the detection and measurement of s are the chief difficulties. In consequence of the Maxwellian distribution of velocities, the s for individual atoms is spread over a range of values and the resulting branches of the split are broader and more diffuse than the original ray. This can be remedied by any method producing a ray of single or narrow range velocity atoms. Any error in the velocity factor ($3.5\ RT$) will be reduced at the same time. Narrowing of the original ray also helps but increases difficulties in detection of the ray by any means. The actual measurement may be made more certainly by any method which takes accurate account of the variation of intensity in the ray, that is, a method which picks out the s of the majority of the atoms. This is not done of course when actual images are received on plates. Resort must be had to detecting devices such as delicate pressure gauges, ionization gauges, etc., the application of which is very doubtful at present.

[5] Sommerfeld, Atombau and Spektrallinien.—4th ed.

The writer wishes to acknowledge the guiding assistance and suggestions of Professors W. H. Rodebush and Jakob Kunz, and also the kindness of the Department of Physics in allowing the use of the large Dubois magnet.

LABORATORY OF PHYSICAL CHEMISTRY,
UNIVERSITY OF ILLINOIS.
June 4, 1926.

THERMAL CONDUCTIVITY OF Li AND Na BY A MODIFICATION OF THE FORBES BAR METHOD[1]

By C. C. Bidwell

Abstract

The bar method of Forbes was modified as follows. The metal rod, centered in a large test tube, was placed in a constant temperature bath and heated by a coil at the upper end. Convection in the tube was stopped by cardboard disks through which the rod was threaded and which were spaced at short intervals along the rod. Temperature gradient was determined by thermo-junctions spaced along the rod. Cooling curves were obtained on smaller lengths of the rod similarly mounted. With mean temperature not exceeding 15° above bath temperature accurate values of k were obtained.

Lithium shows a linear increase in k from 0.15 at 0°C to 0.20 at −200°C, thereafter rising sharply to 1.00 at −246°C. Above 0°C a minimum occurs at +40°C and an increase thereafter to 0.17 at +140°C. Sodium shows a linear increase from 0.28 at −40°C to 0.40 at −240°C. Above −40°C an increase occurs to 0.34 at 0°C and thereafter a decrease to 0.28 at +65°C. The breaks in these lines correspond to breaks previously reported in electrical resistance and thermo-electric power lines for these metals.

Electrical conductivity of Li and Na. To test the Wiedemann-Franz-Lorentz law the resistances of wires of lithium and sodium were measured at temperatures of ice, liquid oxygen and liquid hydrogen. The "constant" $k/\sigma T$ of the Wiedemann-Franz law was found to have at the higher temperatures the value predicted by the Lorentz theory, and to diminish steadily with temperature in accord with more modern theory.

Specific heats of Li and Na. The specific heats of Li and Na were calculated by a comparison of cooling curves. The values found are in agreement with the best previous measurements and are extended to liquid hydrogen temperatures. At the higher temperatures the atomic heats of both metals exceed the Dulong and Petit maximum. It is suggested that this excess is latent heat of crystallization. At the lower temperatures the results do not show agreement with the Debye specific heat equation.

Introduction

THE measurement of the temperature gradient along a bar of metal together with an auxiliary determination of the rate at which heat escapes from each section, obtained by means of cooling curves, makes possible, in theory, a direct computation of thermal conductivity. The method was first used by Forbes[2] and modifications were made later by

[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[2] Forbes, Trans. Roy. Soc. Edin. **23**, 133–146 (1865); **24**, 73–110 (1865).

Mitchell[3] and by Stewart.[4] Since these early observers failed to get precise results, a comparison of their procedure with that used in the present investigation is of interest. Forbes used a wrought iron rod eight feet long arranged horizontally in the open air with one end extending into a bath of molten lead. Temperatures were read by mercury thermometers placed in mercury wells. With a rod one inch in diameter he got values differing by 20% from those obtained with a rod 1.25 inches in diameter. J. C. Mitchell under Tait's direction repeated Forbes' work using the same rod and correcting for the variation in specific heat, which Forbes had ignored, and cooling the far end of the bar in water. With the rod thus cooled values did not agree with those obtained when not cooled, the variation being about 10% sometimes more, sometimes less. Stewart substituted insulated thermo-couples and made an effort to protect the bar from drafts by placing a trough under it. The Encyclopedia Brittainica, 11th Ed., in its discussion of the bar methods, says, "The discrepancies are chiefly due to the error of the fundamental assumption that the rate of cooling is the same at the same temperature under the very different conditions existing in the two parts of the experiment." The use of mercury thermometers and of insulated thermo-junctions must have contributed also to the discrepancies in all this early work.

The Forbes method is departed from in the bar experiments of Callender and Nichols[5] and of Lees[6] in which heat escape from the sides of the bar is eliminated either by lagging or by placing the rod in a vacuum. Callender and Nichols used a bar 4 feet long and with a diameter of 4 inches. One end was placed in steam the other in running water, the rise in temperature of which was measured. Lees used a short rod 8 cm long, .585 cm in diameter, surrounded it with packing and heated one end electrically. The other end was fitted into a copper block. Temperatures at top and bottom of the rod were measured by platinum resistance wires wound on the rod. Schott[7] modified Lees method by placing the rod in a vacuum. Good results were obtained by all these observers.

In the present study wide departures were made from the procedure of the early observers although the method in theory is exactly that of Forbes. The special features to be emphasized are (1) exact duplication of the external conditions in the two parts of the experiment, (2) precise temperature measurements through the use of bare thermo-couples

[3] Mitchell, Trans. Roy. Soc. Edin. **28**, 717 (1879)
[4] Stewart, Phil. Trans. Roy. Soc. London **184A**, 570 (1893)
[5] Callender and Nichols, Ency. Britt. 11th Ed.
[6] Lees, Phil. Trans. **208**, 381 (1908).
[7] Schott, Verh. d. D. Phys. Ges. **18**, 27 (1916).

embedded in the rod and in metallic contact with it, (3) development of the theory leading to equations which fit exactly the experimental conditions and whose terms can be precisely evaluated from the experimental data by graphical or analytical methods.

The metals investigated were sodium, lithium, and single and polycrystal zinc. The present report deals only with the work on sodium and lithium. Rods of these metals 25 cm long and 1.10 cm in diameter, produced by extrusion through a die, were mounted in glass tubes as shown in Fig. 1. A heater coil consisting of about 10 turns of chromel *A*

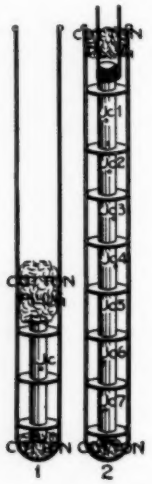


Fig. 1. 1. Arrangement for getting cooling data.
2. Arrangement for getting gradient data.

resistance wire No. 26 was wound on the upper end of the rod but insulated from it by several layers of oiled paper. Copper-constantan thermojunctions (No. 30 wire) were spaced every 3 cm along the rod. The bare junctions were pressed into the soft metal by means of a needle to a depth of 2 or 3 mm and the needle hole closed by squeezing the metal back about the wires. Tissue paper insulation wound on the junction wires insulated them from each other and from the rod. Usually six junctions were placed on a rod. After the junctions were mounted cardboard washers were slipped over the rod and spaced every two cm along the rod. These washers fitted the rod tightly and were of such outer diameter as also to fit snugly the glass tube in which the rod was mounted. They served to center the rod and to cut off convection currents up and down the tube. The glass tube containing the specimen thus mounted was 2.7 cm in diameter, 40 cm in length, and closed at the lower end. The

tube was used in a vertical position with the rod in the lower half. The heater leads and all junction leads were led out through the top of the tube. The tube with the rod thus mounted was placed in a constant temperature bath contained in a Dewar cylinder of 40 cm length and some 7 cm inside diameter. The bath usually extended about 15 cm above the top of the rod. The tube above the rod was stuffed with cotton. (In the case of the liquid hydrogen bath a shorter tube was used, one which did not extend much above the bath level and which therefore did not allow the entrance of air which would have liquified and frozen about the specimen). The constant temperature baths were liquid hydrogen, -252.8°; liquid oxygen, -183°; CO_2 slush, -77.5°; crushed ice, 0°; boiling chloroform, +61°; boiling water, +100°; boiling tetrachlorethelene, +121°.

The rod was allowed to come to the temperature of the bath and the readings of all junctions were taken. Then the rod was heated at the top by means of the resistance coil until the top junction read about 3° or 4° above the bath temperature and the current was adjusted to hold this temperature. Readings of all junctions were taken at intervals until equilibrium was established and no further changes were found to occur. About one hour usually sufficed, although at liquid hydrogen temperature five minutes was sufficient. After all readings were taken the heater current was increased until the top junction read 10° or 15° above bath temperature and the operation repeated. Thus two sets of readings were obtained for each bath. After these data were obtained the rod was, where conditions permitted, removed from the tube and immersed directly in the bath and the readings of each junction obtained, the heater current of course being zero. This gave the reading of each junction for the bath temperature thus permitting discrepancies in junction readings to be determined and taken into account.[8]

For the second parts of the experiment a short rod, in most cases 4 cm long, of exactly the same diameter as the test rod, containing a single junction embedded in it and similarly fitted with cardboard washers, was preheated 60° to 80° above the bath temperature then slipped into the tube and allowed to cool to the bath temperature. Temperatures were read every half minute as the rod cooled. For each bath cooling curves were thus taken on rods of lithium, sodium, copper, lead and

[8] Temperatures along the rod were determined by a method of differences. The difference in microvolts between the bath temperature and the rod temperature as expressed by the same junction was divided by the microvolts per degree for the particular temperature obtained from the calibration equation of the junction. Relative temperatures along the rod were accurate within .05°, although actual temperatures may have been uncertain within one or two degrees.

silver, each rod being of the same dimensions and similarly mounted. To obtain similar surfaces all rods were wound tightly with a single layer of paper. Cooling curves were also obtained with copper and lead rods of 8 cm length. Exactly the same heat loss rate per cm length was obtained in these cases. The determination of the rate of heat loss per cm length is the critical part of the work and for that reason the observations were

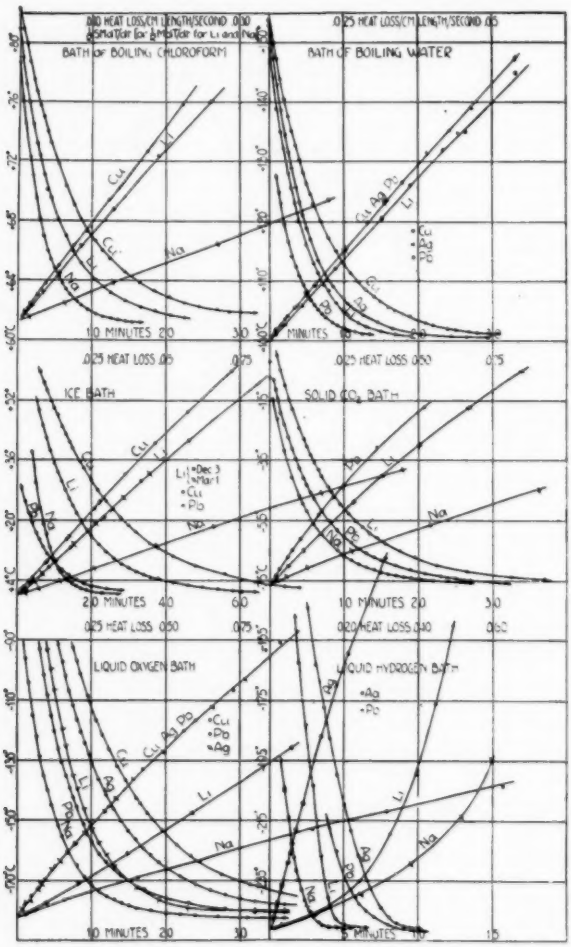


Fig. 2. Cooling and heat loss curves for different metals at various bath temperatures.

obtained on these various metals so that the heat loss curves might be very accurately established. All the rods had the diameter 1.10 cm. A rod of 1 cm diameter gave quite a different heat loss rate per cm length and even per sq cm, apparently because of the longer air path through

which the heat must be carried to the surrounding tube. The same surrounding tube was used in all cases as tubes of slightly different diameters caused serious discrepancies. Cotton plugs above and below the cooling specimen eliminated heat loss from the ends. This was proven by the fact that the heat loss per cm length from the 8 cm rod was exactly the same as from the 4 cm rods. Fig. 2 shows the cooling curves and the heat loss curves derived from them for the different metals and for the various bath temperatures. Rate of heat loss per cm length is computed from the formula $Ms/L \cdot dT/dt$, where L is the length of the specimen, M its mass, s, the specific heat and dT/dt the rate of cooling.

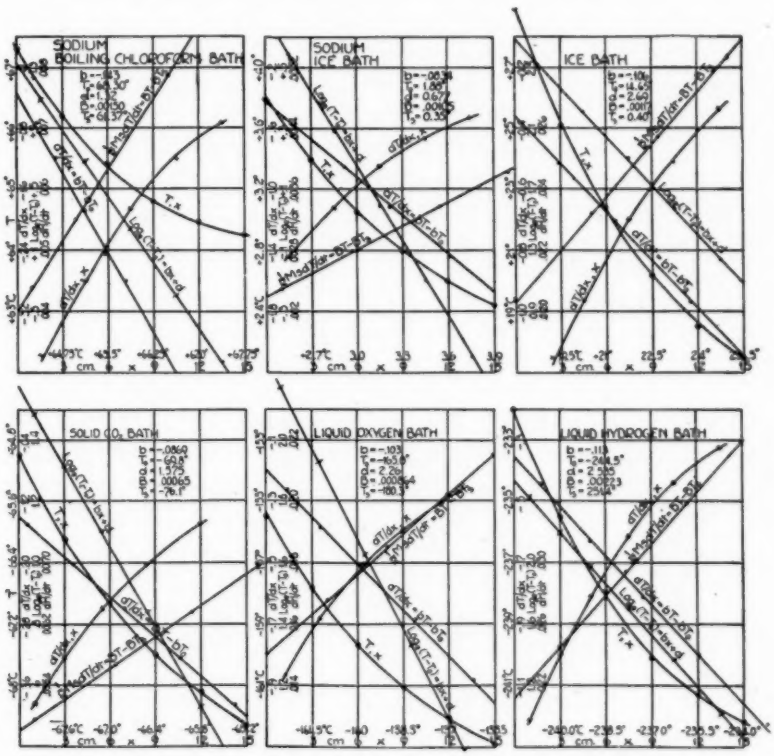


Fig. 3. Gradient data and derived relations for sodium.

Theory of the Method

The difference between the heat which flows through a given section of the rod a distance x_1 from some arbitrary origin near the hot end and that which flows through a section a distance x_2 from the same origin is equal to the heat which escapes from the surface between the two sections. This is expressed by the equation

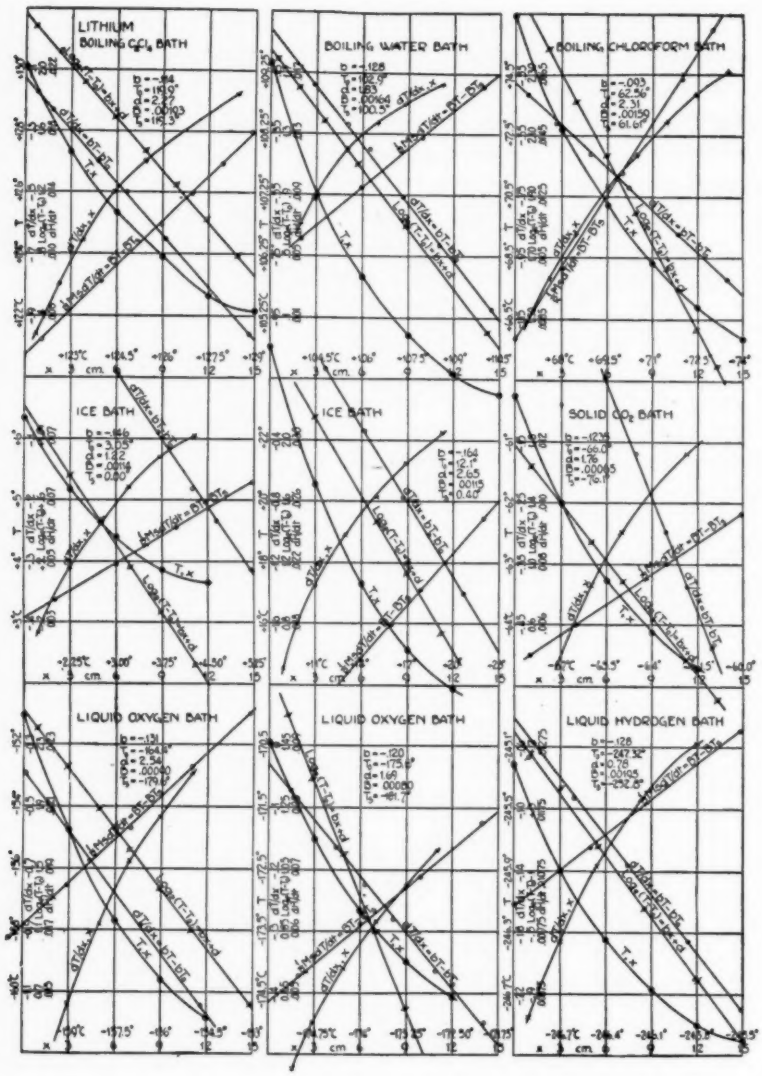


Fig. 4. Gradient data and derived relations for lithium.

$$kA[(dT/dx)_1-(dT/dx)_2]=\int_{x1}^{x2}(dH/dt)dx \qquad (1)$$

k is the thermal conductivity; A, the cross-section of the rod; $(dT/dx)_1$ and $(dT/dx)_2$, the temperature gradients at points x_1 and x_2; (dH/dt), the heat loss per second per cm length. (dH/dt) may be obtained from the cooling data and is given by the expression $dH/dt=Ms/L\cdot dT/dt$. Fig. 2

shows that over short temperature ranges the heat loss curves are sensibly straight lines. The temperature drop along the rods rarely exceeded 10° and in most cases did not exceed 3° whereas the heat loss curves are essentially straight lines over 20° or more. Thus we may write

$$Ms/L\cdot dT/dt = BT + D$$

or

$$Ms/L\cdot dT/dt = BT - BT_s \tag{2}$$

We may call T_s the apparent surrounding temperature. It is the actual surrounding temperature only when the average value of T is within a few degrees of the bath temperature or when the temperature interval is the first interval on the heat loss curve. Eq. (1) now becomes

$$kA[(dT/dx)_1 - (dT/dx)_2] = \int_{x_1}^{x_2} BT\,dx - \int_{x_1}^{x_2} BT_s\,dx \tag{3}$$

Figs. 3 and 4 show T, the temperature along the rod, plotted against x, the distance along the rod measured from the first junction as origin; also dT/dx, the slopes of these lines plotted against temperature. These are shown for the various bath temperatures. The dT/dx, T curves are in all cases straight lines. Therefore

$$dT/dx = bT + a$$

or

$$dT/dx = bT - bT_0 \tag{4}$$

This equation may be written

$$\int dT/(T - T_0) = \int b\,dx \text{ which gives}$$

$$\text{Log}_e(T - T_0) = bx + d \tag{5}$$

or

$$T = e^{bx+d} + T_0 \tag{6}$$

The lines representing Eq. (5) are also shown on Figs. 3 and 4. Using Eq. (6) in (3) we have

$$kA[(dT/dx)_1 - (dT/dx)_2] = \int_{x_1}^{x_2} B[e^{bx+d} + T_0]\,dx - \int_{x_1}^{x_2} BT_s\,dx. \tag{7}$$

This becomes

$$kA[(dT/dx)_1 - (dT/dx)_2] = \frac{Be^d}{b}[e^{bx_2} - e^{bx_1}] + B(T_0 - T_s)[x_2 - x_1] \tag{8}$$

The constants B, d, b, T_0 and T_s of this equation may be obtained graphically from the curves of Figs. 3 and 4. Thus with the gradients known at distances x_1 and x_2, k may be computed.[9]

[9] T_0 (Eq. 4) is the temperature of the rod where the gradient is zero. This has physical significance as such only when the rod is very long or when the mean rod temperature is only slightly above the bath temperature. In such cases $T_0 = T_s$ = bath temperature, and the last term of Eq. (8) vanishes, but with short rods and higher rod temperature, this term is increasingly important.

Results

The values of thermal conductivity, k, as a function of temperature are shown for sodium in Fig. 5 and for lithium in Fig. 6. In the case of lithium

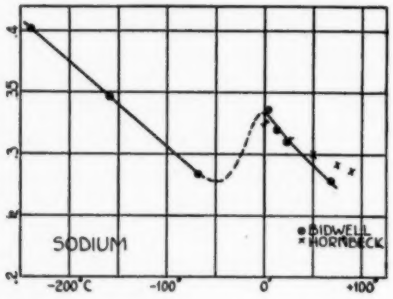


Fig. 5. Thermal conductivity of sodium.

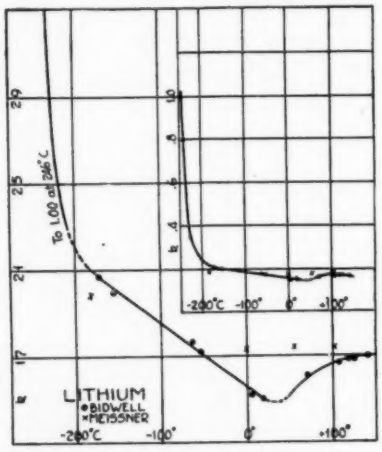


Fig. 6. Thermal conductivity of lithium.

two values were obtained for each bath. In one case the average temperature of the rod was not more than 5° above bath temperature, in the other the average temperature was 10° or 15° above bath temperature. The values of the constants B, d, b, T_0 and T_s are entirely different in the two cases yet the equation gives consistent values for k in each case. We have thus an excellent check on the method and on the computations. The discontinuities shown on these curves, at $-50°$ for sodium and at $+40°$ for lithium are extremely interesting especially in view of the resistance and thermoelectric power behavior in these same regions. Fig. 7 reproduced from a previous paper[10] shows the electrical resistance and thermoelectric

[10] Bidwell, Phys. Rev. **23**, 357 (1924).

power lines for these metals. It will be noted that these lines indicate changes or discontinuities in the same temperature regions. Comparison of Figs. 5 and 6 leads to the view that the change in the case of sodium is practically completed in the region -50° to 0° whereas in the case of lithium the transition is more gradual extending over the range +40° to at least +150° where the value of k seems to have reached a maximum. From the behavior of the sodium line one would predict a decrease in k for lithium above +150°C but data on this are not yet available and

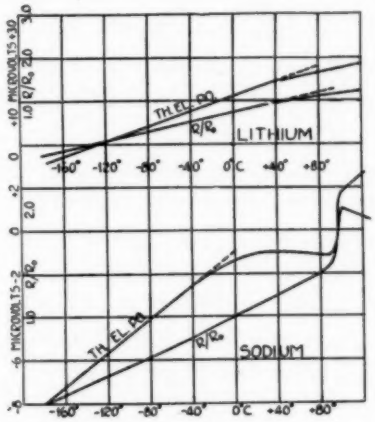


Fig. 7. Electrical resistance and thermoelectric power of lithium and sodium.

are not obtainable by the present method. The discontinuities in these lines are apparently associated with the breakdown of the crystal lattice. That the lattice structure becomes obliterated at the higher temperatures for these metals has been shown by the writer[11]. An increase in thermal conductivity associated with a disintegration of the crystal lattice is an observation which should have a fundamental bearing on the theory of heat conduction.

The Work of Other Observers on Lithium and Sodium

The only other work with which the present observations may be compared is that of Meissner[12] on lithium and Hornbeck[13] on sodium. Both of these observers used the Kohlrausch-Diesselhorst Method. In this method a wire or rod of the metal is mounted in a highly exhausted tube, the ends of the rod or wire kept at constant temperature, and a temperature gradient established by an electric current sent through the

[11] Bidwell, Phys. Rev. **27**, 381 (1926).
[12] Meissner Zeits. f. Physik **2**, 273 (1920)
[13] Hornbeck, Phys. Rev. **2**, 217 (1913).

rod or wire. Hornbeck measured the potential drop between two sections equally distant from the middle and therefore at the same temperature, and the temperature at these points and at the middle. In the stationary state the Joule heating between two points is equal to the difference between the heat flowing into and out of the section. An equation is developed in which the ratio of the thermal to the electrical conductivity is expressed in terms of the voltage drop between the two points at the same temperature and their common temperature and the temperature of the middle of the bar. Meissner used a wire 0.5 mm in diameter and modified the method by using two different currents, developing an equation in which the ratio of the thermal and electrical conductivities is expressed in terms of the voltages at two points equally distant from the middle of the wire, the resistances at the mean temperatures corresponding to the two currents and the temperature coefficient of resistance. Hornbeck's data for sodium extended only over the range 0° to +90°. His values are shown on Fig. 5. These values are in good agreement with mine as to absolute values but the slope of his curve is somewhat smaller. The difference may easily be due to difference in purity or to difference in previous history. My specimen had been cooled repeatedly while his had never been cooled below 0°C. His specimen possibly was in more stable condition than mine with respect to the change which occurs between −50° and 0°. Hornbeck did not extend his observations below 0°C and hence missed noting this change.

Meissner's values for lithium are shown also on Fig. 6. He gives values for k, .1734 at 101°, .1734 at +56°, .1730 at 0°, .197 at −182°, and .493 at −253°. We are in approximate agreement as to absolute values and as to the abnormal increase below −200°C and his data show a slight indication of the peculiar behavior between 0° and +100° but not do bring this out conclusively. His values were obtained by a rather indirect method and required besides resistance and voltage measurements an accurate measurement of the temperature coefficient of resistance. There is a marked difference in the temperature coefficient at 0° and that at 100° as shown by Fig. 7. The change in this quantity unless taken account of might easily produce the discrepancies between his values and mine in this region. In view of my many repeated observations over this range there can be no doubt as to the actual course of the line in this region.

The Wiedemann-Franz-Lorentz Law

In order to test the Wiedemann-Franz law the resistance of wires of sodium and lithium was measured at the temperatures of ice, liquid

oxygen and liquid hydrogen. The wires were formed by squirting through a die and were of the following dimensions: lithium, 90 cm long, .1625 cm diameter; sodium, 51.3 cm long, .2921 cm diameter. They were wound in the form of a spiral and were measured bare. The specific resistance of the lithium at 0° was found to be $.885\times10^{-5}$, and of sodium $.426\times10^{-5}$. The ratio of the resistance at liquid oxygen temperature to that at 0° was found for both metals to be exactly that shown on the curves of Fig. 7. With the relation $\rho/\rho_0=R/R_0$ it is therefore possible to compute specific resistances from these curves for any temperature. Table I shows for various temperatures the values of the thermal conductivity k and the electrical conductivity σ for lithium and sodium and the values of $k/\sigma T$ expressed in c.g.s. units. The Lorentz theory in its simplest form

TABLE I

Values of thermal and electrical conductivities of lithium and sodium.

	Lithium			Sodium			
T°K	k	σ	$k/\sigma T$ (c.g.s.)	k	σ	$k/\sigma T$ (c.g.s.)	(Hornbeck)
423	.170	7.14×10^4	23.6×10^7				
398	.169	7.57	23.6				
373	.166	8.13	23.0				
348	.161	8.70	22.4	.270	17.1×10^4	19.1×10^7	(20.7×10^7)
323	.153	9.44	21.2	.290	18.9	20.0	(20.5)
293	.149	10.35	20.6	.300	21.2	20.0	(20.6)
273	.155	11.55	20.7	.335	23.5	21.9	(21.0)
248	.163	12.85	21.5	....	.....	....	.... ..
223	.170	15.00	21.3	.280	31.4	16.9	
198	.177	17.5	21.4	.288	36.2	16.9	
173	.185	21.1	21.3	.305	43.4	17.0	
148	.192	26.9	20.2	.324	53.5	17.1	
123	.200	36.1	19.0	.340	67.0	17.3	
98	.207	57.8	15.4	.360	93.8	16.4	
73	.218	116.	10.9	.377	133.3	16.3	
33	....	.....	....	.403	226.0	22.6	
23	1.00	1050.	17.3	....	.....	....	

gives $k/\sigma=\pi/2\ (a/e)^2T$, where a is the Boltzmann constant, 2×10^{-16}, and e the electronic charge, 1.59×10^{-20} e.m.u. Thus at 18°C or 291°K the ratio should have the value $k/\sigma T=24.7\times10^7$. The agreement shown in the tables is rather good. The steady diminution in the value of this so-called constant with lowering temperature is in agreement with more modern theory. Hornbeck developes an equation which calls for just such a falling off.

SPECIFIC HEAT OF LITHIUM AND SODIUM

The specific heat may be obtained from cooling curves on the assumption that the heat loss per cm length from rods of different material but

of the same diameter and with same surface (obtained by winding tightly with a single layer of paper) and cooling under exactly the same conditions is independent of the material of the rods and depends merely upon the temperature of the rod and that of the surrounding bath. This assumption has been thoroughly tested with rods of lead, copper and silver. With these metals, when the heat loss per com length per second, given by the expression $Ms/L \cdot dT/dt$ is plotted against rod temperatures, the points all lie on the same curve. (Fig. 2). In the cases of lithium and sodium the specific heat particularly at low temperatures were not sufficiently known to enable the computation of k. Instead of plotting the expression

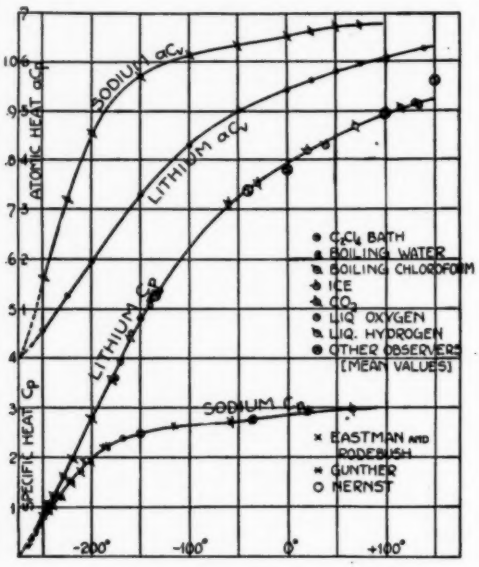


Fig. 8. Specific heat of sodium and lithium.

above for heat loss rate, the expression $ML \cdot dT/dt$ was plotted (Fig. 2). The curves lie to the right of those obtained when s is taken account of, and for any temperature the ratio of the abscissas gives the specific heat. The curves in Fig. 8 show the values of specific heats so obtained. On this plot are shown also the values obtained by other observers. The agreement for both metals is extremely good. Atomic heats aC_v are also plotted, C_v being computed by means of the Nernst-Lindemann equation[14]. For both metals the values of aC_v exceed the DuLong-Petit maximum of 5.95. The lithium values exceed this maximum above +75°C, the sodium values above −125°C. I wish to suggest

[14] Lewis, Physical Chemistry, Vol. III, 67, Longmans.

that *this excess specific heat is possibly latent heat of crystallization, i. e. heat required for the disintegration of the crystal lattice which the evidence indicates is gradually taking place.*

Debye's specific heat equation in the form $aC_v/5.95 = 77.94\ (\theta/\theta_m)^3$ fails to fit the data for these metals. For this test θ_m was taken for lithium as 480° and for sodium at 418° on the assumption that a smooth curve expresses the relation between θ_m and atomic weight. The lithium data partially superposes the curve which has been found to be common for aluminum, copper and silver but lies above it for all the upper range. The sodium curve does not even lie near the common curve, the values of $aC_v/5.96$ being from 50% to 100% high. If the value $\theta_m = 200$ is taken for sodium the fit is about as good as for lithium.

The writer wishes to express his appreciation to Dr. G. K. Burgess for granting the facilities of the Bureau of Standards for these measurements, to Dr. C. W. Kanolt for the preparation of liquid hydrogen in unstinted quantity and for many other courtesies in connection with the conduct of this work at the Bureau, and finally to the Heckscher Foundation for the Advancement of Research for funds which made time available from teaching during the second term of 1925–26 for the carrying out of this work.

CORNELL UNIVERSITY,
May 1926.

BOOK REVIEWS

Le Magnétisme. P. WEISS AND G. FOËX.—The title of this book is more general than its contents warrant. The effects of magnetic fields upon other than magnetic characteristics are not discussed, magnetooptics, magnetoresistance changes and magnetostriction itself being entirely omitted. Instruments and methods of measurement are also ignored. Even in what is included the treatment is notably unequal so that the general reader—to whom, according to the publisher, the book is principally addressed—must derive from it curious misconceptions as to the relative importance of the subjects treated. Magnetic hysteresis, for example, is dismissed with only a few pages, and the whole space devoted to steels for permanent magnets is 18 lines. On the other hand paramagnetism has seldom been treated so exhaustively, 45 consecutive pages being devoted to this subject besides many paragraphs in other places. The key to the anomaly is that the subjects to which the senior author has devoted his life are elaborated and brought up-to-date in a masterly fashion, whereas the connecting tissue is of the slightest. The arguments for the reality of the Weiss magneton, the utility of the concept—also due to Weiss—of the molecular field, the results of experiments by Weiss and his pupils on the ferromagnetism of single crystals (at Zurich), and on the magnetocaloric effect (at Strasbourg) are given here in a most admirable manner, unencumbered by descriptions of the experimental arrangements employed in the various researches. The specialist in magnetism will find the chapters on these subjects of great interest, and will note the inclusion of some hitherto unpublished data. The arguments against the Weiss magneton receive rather less than a fair statement, no notice, for example, being taken of the fact that the observable magnetic moments of atoms and ions should not, on the quantum theory, be integral multiples of the Bohr magneton. On the other hand, the experiments of Gerlach and Stern are treated at some length. The references to prior publications are numerous but many are to theses and a few are defective in form or content. Some papers published as late as the current year are referred to, although less recent experiments of Glaser on the magnetic properties of gases at low pressures are not mentioned. The lack of an index is fairly well supplied by a long table of contents. The use of very small type and of cuts originally prepared for larger pages hinders legibility and there is a distressing number of misprints and lost type, especially in the copious footnotes.—Pp. 215 (16 mo.), 69 figs. Libraire Armand Colin, Paris, 1926. Price, unb. 8 fr. 40;bd.10 fr. 20. L. W. MCKEEHAN

Handbuch der Physik, Band X. [*Thermische Eigenschaften der Stoffe*]. H. Geiger and Karl Scheel.—Under the general editorship of H. Geiger and Karl Scheel, it is planned to publish in twenty volumes a complete survey of the fields of experimental and theoretical physics. Volume X, which is one of the first to appear, is devoted to a consideration of the thermal properties of substances. A list of the titles of the eight chapters in this volume will give the reader a more exact idea as to the nature of the topics discussed. Chapter 1 on Solids is written by E. Grüneisen, Chapter 2 on Fusion, Solidification and Sublimation by F. Körber, Chapter 3 on Gases and Liquids by J. D. van der Waals, Jr., Chapter 4 on Thermodynamics of Mixtures by Ph. Kohnstamm, Chapter 5 on Specific Heat (Theoretical Part) by Erwin Schrödinger, Chapter 6 on Specific Heat (Experimental Part) by Karl Scheel, Chapter 7 on the Determination of Free Energy by Franz Simon, and Chapter 8 on the Thermodynamics of Solutions by Carl Drucker. This list of the authors responsible for the various chapters may serve as an assurance

that the subject matter, in every case, has been treated in a competent manner. We can recommend most highly to the attention of the reader the chapters by Grüneisen, Schrödinger and Scheel. That by Schrödinger, which deals mainly with the applications of quantum theory to the problem of the heat capacities of gases and solids, deserves special commendation, giving, as it does, a concise but masterly treatment of the subject. The chapter by J. D. van der Waals, Jr., is an exhaustive discussion of the van der Waals equation and its possibilities. The reviewer is of the opinion that there are limits to the usefulness of this famous equation and that these limits have been exceeded in the present article. The chapter by Franz Simon on Free Energy is excellent in many respects, but his discussion of the Third Law of Thermodynamics suffers from following too closely the historical development of the subject at the hands of Nernst and his followers. One really does not expect to see a table of Nernst's "conventional" chemical constants in a treatise published in 1926. In conclusion, it may be remarked that a student who may attempt to make himself acquainted with the contents of this volume will find his task measurably increased by the fact that there is no approach to a consistent system of notation or of nomenclature. VI+486 pp., 207 figs., Julius Springer, Berlin. 1926. Unb. 35.40 Rm, bound 37.50 Rm. F. H. MACDOUGALL

Introduction to Theoretical Physics. (Vol. II). ARTHUR HAAS. Translated from the German by T. Verschoyle.—The second volume of Professor Haas' Theoretical Physics is divided into three parts dealing with Atomic Theory, Theory of Heat, and Theory of Relativity respectively. This volume is much less mathematical than the first volume. Thus while the section on atomic theory contains the simple Bohr theory for circular orbits in hydrogen and ionized helium, the theory of the fine structure and that of the Stark effect are dismissed as being beyond the scope of the book. Again the computation of the metric in the region surrounding the sun is omitted as "too involved to be reproduced here" in spite of the considerable space devoted to tenser analysis in the first volume.

On the other hand this volume is very readable. The first section contains an excellent account of the measurement of the charge on the electron, the properties of x-rays and the subject of radioactivity in addition to the simpler aspects of the Bohr theory. The second section treats the theory of heat from the point of view of statistical mechanics. The topics conventionally included under the heading of thermodynamics are followed by Debye's theory of specific heats and the theory of black body radiation. The third section contains a fairly complete account of the main features of the special relativity theory, but the general theory is not treated in sufficient detail to enable the reader to follow through the analysis leading to the observable effects in a gravitational field. An appendix contains a synopsis of the topics discussed in the volume, and such recent developments as the Compton effect are briefly mentioned in addenda. X+414 pp., 130 figs., D. Van Nostrand Company, New York City, 1926. Price $6.00.

LEIGH PAGE

Experimental Optics. G. F. C. SEARLE.—This Manual describes the optical experiments done in the "practical" class at the Cavendish Laboratory. The experiments vary in simplicity from a verification of Snell's Law, and the determination of refractive indices with a microscope to the determination of the pyramidal error of a prism, experiments with compound lenses, and studies of the astigmatism and certain other errors of lenses. Of the seventy experiments described, fifty-six deal with geometrical optics, which includes work with spectrometers and the behavior of lenses and mirrors. The last two chapters deal primarily with interference and the plane diffraction grating. The title of the book is somewhat misleading, as the book does not consider the subjects of spectrometry, photometry, radiation, and of polarization (except for a single experiment on the determination of a polarizing angle), and as it contains no treatment of the concave grating and of the other instruments of high resolution for the study of spectra.

For the most part, the apparatus required for the experiments is ingenious and not elaborate, and the book, therefore, should be very valuable to students and instructors in optical laboratories in our colleges. The discussions which accompany the experiments are likely to be of assistance, especially as some of them contain information which would not be readily accessible elsewhere. The book is written from Mr. Searle's personal experience at the Cavendish Laboratory, and gains thereby an individuality which adds greatly to the value of the work. Pp. xvi+357, 237 figs. Cambridge University Press, 1925. T. T. SMITH.